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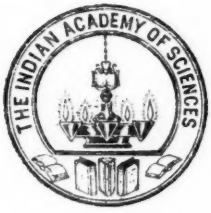

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NOTE ON THE CORRESPONDENCE BETWEEN THE CLASSICAL AND QUANTUM THEORIES OF NEUTRAL MESONS

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Received April 4, 1941

When one speaks of correspondence between the quantum and the classical theories of radiation, one means that the quantum theory of radiation passes over in the limit $\hbar \to 0$ into the classical theory of radiation as embodied in the Maxwell equations. At the same time the formula for any physical process goes over into the corresponding classical formula. This is the strict mathematical sense in which one can speak of correspondence.

It is, however, common to speak of correspondence in another looser sense, thereby referring to the circumstance that the quantum formulæ for several physical processes go over into the corresponding classical formulæ when the energy of the light quantum concerned is small compared with some other constant of the dimension of energy occurring in the formulæ. A typical example of correspondence in this loose sense is afforded by the scattering of light by a free electron, where the quantum formula given by Klein Nishina goes over into the classical Thomson formula when the frequency of light is small.

In the quantum theory of radiation, the energy E of a light quantum of frequency ω is given by

$$E = \hbar\omega. \tag{1}$$

The limit $\hbar \to 0$ therefore corresponds to the limit $E \to 0$, if the frequency be kept constant. Thus the alteration in the quantum formula for any process introduced by going to the limit $\hbar \to 0$ is the same as the alteration introduced by going to the limit of very low frequencies $\omega \to 0$. It is due to this cause that the looser meaning of the word correspondence coincides in most cases with the strict meaning given at the beginning.

The purpose of this note is to point out the interesting circumstance that whereas there is correspondence between the quantum and the classical theories of neutral mesons in the strict mathematical sense, meaning thereby that the former theory goes over into the latter if we pass to the limit $\hbar \to 0$, there is no correspondence between the two theories in the looser sense

A1

outlined above. The reason for this is the following. The classical theory of mesons contains a characteristic constant χ of the dimension of a reciprocal length, but there is no quantity in the classical theory which can be identified with the rest mass μ of the meson. It is only when the theory is quantized that a constant μ, defined by

$$\mu \equiv \hbar\chi \tag{2}$$

is introduced which can be identified with the rest mass of the neutral meson. (The velocity of light has been put equal to unity in this paper.) Further, in the quantum theory a free meson has associated with it an energy E and a momentum p connected with the frequency ω_0 by the relations

$$\begin{aligned} \mathrm{E} &= \hbar\,\omega_0 \\ p &= \hbar\,(\omega_0^2 - \chi^2)^{\frac{1}{2}}. \end{aligned} \tag{3}$$

Now, it can be shown that the quantum theory of neutral mesons goes over exactly into the classical theory if we proceed to the limit $\hbar \to 0$. Equations (2) and (3) show that this limit not only corresponds to the limit $p \to 0$, but also to $\mathrm{E} \to 0$ and $\mu \to 0$. This same limiting state cannot be achieved as in the theory of radiation by going to low frequencies, while giving to $\hbar$ its actual value, for the lowest value which can be given to the frequency ω_0 of a free meson is χ, and then by (3) $p = 0$, but $\mathrm{E} = \mu$, and μ retains its actual value defined by (2). Now μ may occur explicitly in the quantum formula for any given physical process, whereas the classical limit $\hbar \to 0$ corresponds by (2) to the limit $\mu \to 0$, as mentioned above. Thus we *cannot* expect the quantum formula for any given process to go over into the corresponding classical formula by only going to the limit $p \to 0$ in which the momentum properties of the meson are negligible. There is therefore correspondence between the quantum and classical theories of neutral mesons in the strict mathematical sense, but not in the looser sense mentioned above.

As an illustration of the position outlined above, consider the scattering of neutral mesons by a proton or neutron due to the g_1 interaction. Put $g_2 = 0$ for simplicity. The differential cross-section for the scattering of a meson of momentum p and energy E through an angle θ into the solid angle $d\Omega$ in which the incident as well as the scattered meson is longitudinally polarised has been calculated by Booth and Wilson (1941, referred to in this paper as A, formula 15) and is

$$\begin{aligned} d\phi\,(l \to l) = \frac{2\,g_1^2\,\mu^4\,d\,\Omega}{\mathrm{D}} [&8\,\mathrm{E_N}^4 \cos^2\theta + 2\,\mathrm{E_N}^2\,\{\mu^2 \sin^2\theta \\ &+ p^2\,(1 - 2\cos\theta - 7\cos^2\theta)\} + 2\,\mathrm{E_N E} p^2 \sin^2\theta\,(1 - \cos\theta) \\ &- p^2\,(1 + \cos\theta)^2\,\{\mu^2\,(1 - \cos\theta) - 2\,p^2\cos\theta\}], \end{aligned} \tag{4}$$

where
$$E_N \equiv (M^2 + p^2)^{\frac{1}{2}},$$
$$E_i \equiv E_N + E,$$
$$E_i' \equiv E_N - E, \tag{5}$$
and
$$D \equiv E_i^2 (E_i^2 - M^2)^2 [E_i'^2 - M^2 - 2p^2 (1 + \cos\theta)]^2,$$

M being the neutron mass. For $p \ll \mu$, (4) reduces (A 18) to

$$d\phi\,(l \to l) = \frac{4 g_1^4 M^2 (4 M^2 \cos^2\theta + \mu^2 \sin^2\theta)}{(M+\mu)^2 (4M^2 - \mu^2)^2}\, d\Omega. \tag{6}$$

To proceed strictly to the classical limit, we must express E, p and μ in (4) in terms of ω_0 and χ by using (2) and (3) and then go to the limit $\hbar \to 0$. Thus remembering (5) and keeping only the lowest powers of $\hbar$ in every case, in the limit $\hbar \to 0$ we find that $E_N \to M$, $E_i \to M$, $E_i' \to M$, and

$$E_i^2 - M^2 = (E_N^2 - M^2) + 2 E_N E + E^2 \to 2 M \hbar\omega_0$$
$$E_i'^2 - M^2 - 2p^2 (1 + \cos\theta) = (E_N^2 - M^2) - 2 E_N E + E^2 - 2p^2 (1 + \cos\theta) \to -2 M \hbar \omega_0$$
$$D \to 16 M^6 \hbar^4 \omega_0^4.$$

Thus, neglecting terms which vanish when $\hbar \to 0$, only the first term in the square brackets in (4) gives a non-vanishing contribution and (4) reduces to

$$d\phi\,(l \to l) = \left(\frac{g_1^2}{M}\right)^2 \frac{\chi^4}{\omega_0^4} \cos^2\theta\, d\Omega, \tag{7}$$

which is *exactly* the cross-section for this case given by the classical theory as developed in a previous paper (Bhabha, 1939, referred to in this paper as B) if we neglect there the effects of radiation reaction.

Similarly, for the cross-section for the transition in which the incident meson is longitudinally polarised and the scattered meson transversely polarised, Booth and Wilson find (A 19)

$$d\phi\,(l \to t) = \frac{2 g_1^4 \mu^2\, d\Omega}{D} [8 E_N^4 E^2 \sin^2\theta + \text{terms containing lower powers of } E_N]. \tag{8}$$

For $p \ll \mu$, according to Booth and Wilson (A 21), this reduces to

$$d\phi\,(l \to t) = \frac{4 g_1^4 M^2 [4 M^2 \sin^2\theta + \mu^2 (1 + \cos^2\theta)]}{(M+\mu^2)(4M^2 - \mu^2)^2}\, d\Omega. \tag{9}$$

The classical limit of formula (8) is got as before by using (2) and (3) to express E, p and μ in terms ω_0 and χ, and then going to the limit $\hbar \to 0$.

Only the first term in the square brackets in (8) gives a non-vanishing contribution and we find

$$d\phi\,(l\rightarrow t)=\left(\frac{g_1^{\,2}}{\mathrm{M}}\right)^2\frac{\chi^2}{\omega_0^{\,2}}\sin^2\theta\,d\Omega, \tag{10}$$

which is again exactly the classical cross-section for this case.

Finally, the cross-section for the transition in which the meson is initially and finally transversely polarised is according to Booth and Wilson (A 22)

$$d\phi\,(t\rightarrow t)=\frac{g_1^{\,4}d\Omega}{\mathrm{D}}\,[8\,\mathrm{E_N}^4\,\mathrm{E}^4\,(1+\cos^2\theta)$$
$$+\text{ terms containing lower powers of }\mathrm{E_N}]. \tag{11}$$

For $p \ll \mu$ this reduces to (A 24)

$$d\phi\,(t\rightarrow t)=\frac{2\,g_1^{\,4}\,\mathrm{M}^4\,[4\,\mathrm{M}^2(1+\cos^2\theta)+\mu^2\,(3-\cos^2\theta)]}{(\mathrm{M}+\mu)^2\,(4\,\mathrm{M}^2-\mu^2)^2}\,d\Omega. \tag{12}$$

If we go to the limit $\hbar\rightarrow 0$, only the first term in the square brackets in (11) gives a non-vanishing contribution and we get

$$d\phi\,(t\rightarrow t)=\left(\frac{g_1^{\,2}}{\mathrm{M}}\right)^2\frac{1+\cos^2\theta}{2}\,d\Omega, \tag{13}$$

which is once again the corresponding classical cross-section.

Adding (7) and (10) after integrating them over all angles we get the total cross-section for the scattering of a longitudinally polarised meson, namely,

$$\phi_{\text{ long}}=\frac{8\pi}{3}\left(\frac{g_1^{\,2}}{\mathrm{M}}\right)^2\left(1+\tfrac{1}{2}\frac{\chi^2}{\omega_0^{\,2}}\right)\frac{\chi^2}{\omega_0^{\,2}}, \tag{14}$$

which is precisely the cross-section given in B (formula 43) if we neglect there the terms representing the effects of radiation reaction. Similarly, adding the cross-section (10) divided by 2 [to allow for the fact that (10) represents a transition from the initial longitudinal state to the *two* final transverse states] to (13) and integrating over all angles we get the total cross-section for the scattering of a transversely polarized meson, namely

$$\phi_{\text{ trans}}=\frac{8\pi}{3}\left(\frac{g_1^{\,2}}{\mathrm{M}}\right)^2\left(1+\tfrac{1}{2}\frac{\chi^2}{\omega_0^{\,2}}\right), \tag{15}$$

which is again the corresponding cross-section given in B (formula 42).

The above example shows clearly that whereas the general quantum scattering cross-sections (4), (8) and (11) go over exactly into the corresponding classical cross-sections (7), (10) and (13) when $\hbar \rightarrow 0$, the cross-sections got by merely going to the limit $p \rightarrow 0$ namely (6), (9) and (12) are

different from these classical cross-sections. Naturally putting $\mu = 0$ in (6), (9) and (12) makes these coincide with (7), (10) and (13) respectively if we put $\omega_0 = \chi$ in the latter, as we should expect, since (6), (9) and (12) are the cross-sections for the case $p = 0$, *i.e.*, by (3) $\omega_0 = \chi$.

In another paper (Bhabha and Madhava Rao, 1941) it has been shown that there is also complete correspondence between the scattering due to the g_2 term (spin interaction) as given by the quantum and classical theories of neutral mesons, the scattering having the same dependence on energy, scattering angle, and polarisation of the incident and scattered meson in both theories.*

Thus, although there is strict correspondence between the classical and quantum theories of neutral mesons in the sense that the former theory is the mathematical limit of the latter when $\hbar \to 0$, nevertheless it would not in general be possible to use the classical theory to calculate accurately the cross-section for any given process, even in the limit of very small momenta, due to the explicit appearance of μ next to M in the formulæ [*cf.* for example (6), (9) and (12)], for theoretically M and μ have no connection and μ could be greater than M. That we can in fact use the classical theory to a very great extent is entirely due to the fortunate circumstances that with the actual values of the constants as they occur in nature

$$\mathrm{M} \gg \mu \equiv \hbar\chi. \tag{16}$$

Thus neglecting quantities of the order μ/M, *i.e.*, with an error of about 10%, we should expect classical theory to describe physical processes correctly for momenta which are small compared with M.

The above result has an important bearing on the interaction of the meson field with the electron and neutrino. To explain the β-decay, this interaction is formulated exactly on the lines of the interaction of the meson field with the heavy particles, except that the constants g_1 and g_2 are now given much smaller values. The above arguments now show that in no circumstances could a classical theory give any correct indication of processes involving the interaction of mesons with light particles, since the neutron mass M would now be replaced by the electron mass m, and with the actual values of the constants as they occur in nature

$$m \ll \mu \equiv \hbar\chi. \tag{17}$$

* The quantum formula is larger than the classical by a constant factor 3, but it can be shown (*loc. cit.*) that this is entirely due to differences in the averaging over the initial orientations of the spin of the heavy particle in the two theories and is precisely what we should expect from theoretical reasons.

Although, strict mathematical correspondence exists between the classical and quantum theories even in this case, the classical limit $\hbar \to 0$, corresponds to the limit $\mu \to 0$, and hence to a reversal of the inequality (17). Thus the classical theory would in practice lead to quite incorrect results in the interaction of mesons with electrons or neutrinos.

For the reasons stated above, it can nevertheless be used with considerable accuracy to calculate processes involving the interaction of mesons with the *heavy* particles for energies which are small compared with the rest energy of the *heavy* particles, namely, 10^9 e.V.

Summary

The classical theory of mesons only contains the fundamental constant χ. The rest mass μ of the meson is introduced only when the theory is quantized by the relation $\mu = \hbar\chi$. As a result, although the quantum theory goes over strictly into the classical theory when $\hbar \to 0$, the classical theory corresponds not only to the limit in which the momentum properties of mesons can be neglected, but also to the limit $\mu = 0$ (but χ a finite constant). Due however to the fortunate circumstance that in nature $M \gg \mu$ (M being the neutron mass) the classical theory can be used extensively to calculate processes involving mesons and heavy particles, but is entirely inadequate for calculating processes involving mesons and electrons or neutrinos, just because here $\mu \gg m$ (m being the electron mass).

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SYNTHESIS OF 7-HYDROXY-5-METHYLCOUMARIN

By K. Ranganatha Rao and T. R. Seshadri

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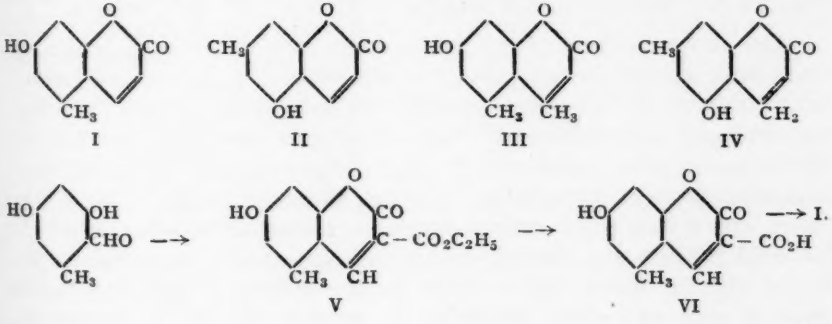
Received January 28, 1941

By the condensation of malic acid with orcinol Pechmann and Welsh[1] obtained a compound to which they assigned the formula of 7-hydroxy-5-methylcoumarin (I) from its similarity with umbelliferone. This was supported by alkali fission of the product whereby orcylic aldehyde was formed. Subsequently Pechmann and Cohen[2] effected the condensation of ethyl acetoacetate with orcinol and the resulting substance was given the constitution of 7-hydroxy-4 : 5-dimethylcoumarin (III) from considerations of analogy. This compound was later investigated by Dey[3] who definitely proved that it was 5-hydroxy-4 : 7-dimethylcoumarin (IV). As a result of this work there has been a tendency to regard the malic acid condensation product also as a 5-hydroxy-coumarin derivative[4] (II). The synthesis of 5-hydroxy-7-methylcoumarin (II) starting from ethyl hæmatommate has been described in a recent communication from these laboratories.[5] This compound is very different from the one obtained by Pechmann and Welsh; its solutions in alkali and in sulphuric acid are deep yellow in colour without fluorescence. Consequently the product of the condensation of orcinol and malic acid should be 7-hydroxy-5-methylcoumarin (I). However strict proof of its purity and individuality has been lacking. This is particularly important in view of the alternative ways in which orcinol can react. Though certain derivatives of 7-hydroxy-5-methylcoumarin have been obtained[6,7] the parent compound itself has not been produced synthetically by unambiguous methods. Attempt



has, therefore, been made now to prepare it from orcylic aldehyde which has been condensed with diethyl malonate. The coumarincarboxylic ester (V) thereby obtained has been hydrolysed to the carboxylic acid (VI) and finally decarboxylated to yield 7-hydroxy-5-methylcoumarin (I). This is identical in every respect with the coumarin obtained from orcinol and malic acid by the method of Pechmann.

Thus it is clear that orcinol behaves in two different ways in regard to its nuclear reactivity when forming coumarins in the presence of sulphuric acid as the condensing agent. With ethyl acetoacetate the γ-position between the two phenolic hydroxyl groups is the reactive centre whereas when malic acid is employed the β-position becomes reactive. And as far as one could judge from the existing data, the γ-position seems to be reactive to the complete exclusion of the β- and *vice versa*. The recent discovery of Desai and Vakil that in the case of Friedel and Crafts reaction orcinol exhibits simultaneous reactivity of the two positions may here be mentioned.[8]

Experimental

7-Hydroxy-5-methyl-3-carbethoxy-coumarin.—Orcylic aldehyde required for this synthesis was prepared by a modification of the method of Gattermann[9] using zinc cyanide. Orcinol (6 g.), dry ether (100 c.c.) and zinc cyanide (15 g.) were placed in a three-necked flask which was provided with a stirrer, a condenser and an inlet for dry hydrogen chloride. The mixture was saturated with the gas; during this process cooling with ice was employed and gentle stirring was kept up. The zinc salt gradually disappeared and the aldimine hydrochloride separated first as a thick oil which slowly solidified (45 minutes). The current of hydrogen chloride was continued for 4 hours. The flask was then sealed and kept in an ice chest for 2 days, at the end of which the solid was collected, washed with ether and decomposed by heating with water. When recrystallised from alcohol, orcylic aldehyde was obtained as colourless needles melting at 182–83°, the yield being 6·5 g.

The above aldehyde (1 g.) and malonic ester (2 g.) were intimately mixed and cooled in ice. To this piperidine (10 drops) was added and the mixture was allowed to stand for an hour in the ice-bath. Cooling was necessary since there was evolution of heat during the addition of piperidine and resin formation took place. The reaction was then allowed to proceed at room temperature for about 12 hours and the mixture was treated with a little dilute hydrochloric acid, cooling in ice being employed. The solid product was filtered, washed with water and recrystallised from alcohol when it yielded shining yellow needles melting at 193–94°. It dissolved in aqueous sodium hydroxide to produce an intense blue-violet

fluorescence. No colour was obtained with ferric chloride. It fluoresced remarkably blue even in neutral alcoholic solution. (Found: C, 58·7; H, 5·5; $C_{13}H_{12}O_5$, H_2O requires C, 58·6; H, 5·3%.)

7-Hydroxy-5-methyl-3-carboxy-coumarin.—The above ester (1 g.) was dissolved in 8% sodium hydroxide (20 c.c.) and allowed to stand for about 3 days. Excess of dilute hydrochloric acid was then carefully added, the mixture being cooled in ice. The precipitated acid was collected and was purified by dissolution in aqueous sodium carbonate and subsequent re-precipitation. Finally it was crystallised from alcohol when it yielded glistening yellow needles melting at 240° (decomp.). It dissolved in aqueous sodium hydroxide to exhibit an intense blue-violet fluorescence. No colour reaction was obtained with alcoholic ferric chloride. It fluoresced bright blue even in neutral alcoholic solution. (Found: C, 55·2; H, 4·5; $C_{11}H_8O_5$, H_2O requires C, 55·5; H, 4·2%.)

7-Hydroxy-5-methyl-coumarin.—The above acid (0·2 g.) was heated with quinoline (4 c.c.) and copper bronze (0·3 g.) for ¾ hour at 150–60° in an oil-bath. The mixture was treated with excess of ether and the solution quickly filtered. Ether was then distilled off; to the residue excess of dilute hydrochloric acid was added and the mixture repeatedly shaken with ether. The ether extract was washed free from acid with sodium bicarbonate solution and then evaporated. The resulting solid was washed with a little benzene to remove resin and crystallised from alcohol. It was obtained as pale yellow flat needles and tablets melting at 247–48°. It was insoluble in water, chloroform and benzene and readily soluble in alcohol, acetone and acetic acid. It gave no colour with alcoholic ferric chloride and its solutions in aqueous sodium hydroxide and in concentrated sulphuric acid were colourless exhibiting blue fluorescence. The coumarin obtained by Pechmann's method using orcinol and malic acid was found to be identical with this compound by a comparison of the properties and by the determination of the mixed-melting point; no depression was observed. (Found: C, 68·2; H, 4·9; $C_{10}H_8O_3$ requires C, 68·2; H, 4·5%.)

Summary

7-Hydroxy-5-methylcoumarin has been synthesised from orcylaldehyde by condensation with diethyl malonate and by subsequent removal of the carbethoxyl group. The compound obtained from orcinol and malic acid by the method of Pechmann has been shown to be identical with the above product and hence it is concluded that in this case orcinol exhibits reactivity of the β-position.

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THE KINETICS OF THE OLEFIN-BROMINE REACTION

Part III. A Note on the Influence of Different Catalysts on the Reaction

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(Communicated by Dr. S. V. Anantakrishnan)

In Parts I and II[1,2] of this series a tentative chain mechanism was suggested to explain the pronounced catalytic influence of even small quantities of hydrogen bromide. Antimony tribromide appeared to exert a retarding influence. This retardation was attributed to the probable removal of hydrogen bromide, an important factor for the propagation of chains, as $HSbBr_4$ or H_2SbBr_5. Before deciding on the mechanism required to explain the course of the reaction, experiments with other catalysts like stannic bromide, bismuth bromide and pyridine, which form definite compounds with hydrogen bromide were considered necessary. The present work deals with the effect of a few promoters and possible inhibitors on the rate of addition of bromine to $\beta\beta$-dimethylacrylic acid in acetic acid.

Table I

Influence of catalysts on the rate of addition of bromine to $\beta\beta$-dimethyl acrylic acid in acetic acid

(*Concentration of reactants*: $M/60$; $t = 36{\cdot}5°$ C.)

Catalyst	Catalyst Reactants	Time (mins.) taken for % reaction 15%	20%	25%
..	..	39·4	54·3	71·3
HBr ..	0·11	31·3	44·2	58·3
$BiBr_3$ ..	0·20	21·8	28·8	36·5
,, ..	0·10	29·0	39·5	50·3
Pyridine ..	0·20	22·5	33·0	48·0
	0·10	33·8	49·7	68·2
$SnBr_4$ ..	0·20	30·5	43·8	59·2
	0·10	37·2	51·8	68·4
$SbBr_5$ ..	0·20	37·5	53·2	71·0
	0·10	42·0	58·6	77·0

Examination of Table I clearly shows that bismuth bromide, pyridine, stannic bromide and antimony pentabromide function as positive catalysts when present in sufficient amounts. When present in the same molar percentage with respect to the reactants, the activity decreases in the order mentioned.

With antimony pentabromide the effect is almost negligible even when the molar percentage of the catalyst is as high as 20% with respect to the reactants. As already indicated in Part I[1] the difference in the degree of activity when present in equimolar concentrations, is clear evidence for the existence of a catalyst reactant complex[5] the difference depending upon the extent of formation and stability of the complex.

Control experiments with the tribromides of antimony and arsenic showed interesting results (*vide* Table II). They showed that there is an immediate

TABLE II

Effect of tribromides of arsenic and antimony on the rate of addition of bromine to ββ-dimethylacrylic-acid in acetic acid

(*Concentration of the reactants M*/60; $t = 35{\cdot}5°$ C.)

Catalyst	Catalyst	Time (mins.) taken for % reaction		
	Reactants	15%	20%	25%
$SbBr_3$ ..	0·2	43·0	60·7	80·0
	..	54·0	73·0	94·5
$SbBr_3$ ..	0·1	42·5	59·0	77·4
	..	46·8	63·7	82·2
$AsBr_3$ ..	0·2	42·7	60·0	82·0
	..	52·0	70·0	91·0
$AsBr_3$ ..	0·1	39·2	55·5	75·0
	..	46·0	62·8	81·0

Note.—In the uncatalysed reactions the bromine concentration was adjusted to be the same as in the catalysed ones, where part of the bromine is removed by compound formation.

formation of an equivalent amount of the pentabromide in the case of antimony compound. With arsenic tribromide, however, there was a fall in concentration of "available" bromine, this diminution being a function of concentration. No pentabromide of arsenic is described in literature[7]

but the present observations can be explained only by assuming the existence of an equilibrium of the type

$$AsBr_5 \rightleftharpoons AsBr_3 + Br_2.$$

The existence of such a compound in solution is being investigated by physical studies.*

The apparent retardation noticed in the earlier work is obviously due to a decrease in the bromine concentration, the effect being more noticeable in the case of slower reaction with crotonic acid. The absence of a negative catalyst, however, does not rule out a chain mechanism for the reaction. Also, it has to be observed that with small concentrations of catalysts of moderate efficiency (*e.g.*, $SnBr_4$, $SbBr_5$) the influence is small being sensibly the same up to about 5% in the present series.

In Part I[1] it was shown that, the uncatalysed reaction values of k_2 tended to increase in the early stages of reaction. Calculation of k_2 values for the catalysed reactions (Table II) showed that k_2 falls gradually to a constant value with increase of the catalyst concentration, further increase resulting in falling k_2 values. This is only in conformity with the observed "velocity —catalyst concentration" curve (*loc. cit.*).

The existence of several catalysts of comparable as well as of varying efficiency for this reaction brings it into line with other similar additive reactions. In all the cases an explanation of the course of the reaction involved the postulate of a catalyst reactant complex, whose stability varied with the catalyst. For instance, using a chain mechanism Mayo and Walling[6] have explained the addition of hydrogen halides and bisulphites to alkenes. Further support is also forthcoming from the recent studies on the high temperature chlorination of olefins by Rust and Vaughan.[8]

It is significant to note that the addition of bromine to $\alpha\beta$-unsaturated aliphatic acids is unaffected by the presence of peroxides[6] so that though dissolved oxygen was not excluded in the present work, the results are not likely to be vitiated by any such effect. Apparently such influence is noticed only with addenda of Class II of Ingold's classification.[3]

Experimental

The reactions were carried out as described in Part I of this series[1]. Bromine, acetic acid, $\beta\beta$-dimethyl acrylic acid and antimony tribromide were purified as in Part I.

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* *Note added in proof*:—Magnetic Susceptibility Studies by Miss K. Savithri also indicate the presence of $AsBr_5$ in solution (*Private Communication*).

Bismuth Bromide.—Hopkin and Williams' purest sample was dried in vacuum over phosphorus pentoxide for several days and taken just before use.

Antimony Pentabromide.—Equal volumes of equimolar solutions of purified antimony tribromide and bromine were mixed and diluted to the required concentration.

Arsenic Tribromide.—The Kahlbaum sample was distilled under low pressure, rejecting large head and tail fractions. It was further purified by solidification by immersing in ice-water, and rejecting the first melt. The operation was repeated until a sample of constant melting point (31° C.) was obtained.

Stannic Bromide.—Kahlbaum purest sample was further purified by the same method as arsenic tribromide, m.p. 30° C.

Pyridine.—Kahlbaum sample was purified by the method of Heap, Jones and Speakman.[4] The resultant liquid was distilled, collecting the middle fraction, b.p. = 115° C.

The author wishes to acknowledge his indebtedness to Dr. S. V. Anantakrishnan for his valuable guidance throughout the work.

Summary

When present in sufficient amounts, different catalysts have been shown to influence the addition of bromine to dimethylacrylic acid in varying degrees. No negative catalysts have been found so far.

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A STUDY OF THE CHEMICAL COMPONENTS OF THE ROOTS OF *DECALEPIS HAMILTONII* (MAKALI VERU)

Part II. A Note on the Preparation of Inositol by Solvent Extraction

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Received February 4, 1941
(Communicated by Prof. T. R. Seshadri)

In a previous communication was described the general chemical composition of the roots of *Decalepis Hamiltonii*. From the petroleum extract of the dry roots the isolation of resinols, sterols, fatty acids and an essential oil consisting mostly of *para* methoxysalicylicaldehyde was reported. The subsequent alcoholic extract yielded saponins, tannins and resin acids besides small quantities of inactive inositol. It was also observed that the roots tasted sweet and that this sweetness was very marked in the dry samples. Larger quantities of inositol were therefore expected to be present in this plant than what the early experiments indicated. Hence experiments have been carried out with a view to evolve a new and efficient method of extraction and the results are embodied in this paper.

Inositol seems to be widely distributed both in the vegetable and animal kingdoms and is stated to be the starting material for the synthesis of more complex compounds. However its rôle in the animal and plant metabolism is still obscure. The presence of isomeric forms of inositol was noted in the leaves and water of some species of Cocos[2] and also in fishes.[3] The muscles, flesh and blood of many animals are stated to contain it either in a free or combined state. However these are poor and inconvenient sources. For its isolation in quantity, wheat bran has been employed and found to be not quite suitable.[4] Herein inositol exists as phytin and can be precipitated as the calcium or the barium salt. The precipitate is then hydrolysed with mineral acids at elevated temperatures to produce inositol. The processes involved are complex and the equipment required is rather elaborate. The yield is only 0·52%. Though the preparation has to follow the same lines, the steep waters of the starch industry have been found to be quite suitable as the starting material for the production of inositol. The yield in this case is reported to be 12·52% on the dry phytin precipitate.[5]

Monomethyl ethers of both *d* and *l* inositol occur in certain varieties of rubber latex and can be obtained from the serum after coagulation. The

isolation of quebrachitol (*l*-monomethyl ether of inositol) on a large scale[6] from this source involved many chemical engineering problems, and the yield of it was found to be about 20 pounds for 1,000 gallons of the serum processed.

Attempts have all along been made to make inositol cheap with a view to stimulate research and to employ it in industrial processes. It has been tried as a base for the manufacture of synthetic resins[7] and its hexanitrate has been patented as a detonating agent.[8] If available at a low cost inositol could be used in the preparation of bacteriological media. Weiss and Rice[9] have suggested that by the use of inositol it is easy to differentiate between various strains of bacteria.

When inositol occurs free, in order to isolate it, the alcohol or the aqueous extract of the material is treated with basic lead acetate and the precipitated lead compound is further worked up. This method has been found to be unsuitable in the case of the *Decalepis* roots. It was not only time-consuming but the yield was also poor being only 0·01% on the weight of the air-dried roots. After a number of trials it has been discovered that it is possible to get high yields by suitable extraction with solvents alone. With a view to effect the removal of waxy and other matter that are likely to interfere with the final isolation of inositol various solvents have been examined for preliminary extraction and light petroleum has been found to be the best. The procedure is simple and very satisfactory. From the wax-free residue of the root methyl alcohol readily extracts inositol in a fairly pure condition. In order to improve the efficiency of the extraction it is desirable to employ methyl alcohol containing a little water. The details of the method are given below:

2 Kg. of the air-dried root powder were exhaustively extracted with petroleum ether for about 20 hours in a Soxhlet extractor. This treatment removed the oily and fatty matter completely from the material and the last traces of the solvent were removed by blowing air through it. Subsequently it was extracted with methyl alcohol. The first five syphonings were coloured brown and hence the extract up to this stage was collected separately (A). Then the extraction was continued with the same solvent for 15 hours and during this process the addition of 10% of water to the solvent improved the extraction of inositol to a considerable degree. The extract was concentrated by distilling off the major bulk of the solvent and set aside undisturbed for a day. Inositol separated out at the bottom of the container in a well-defined crystalline form and was recovered by filtration. The crude product was dissolved in 50 c.c. of boiling water and the insoluble

impurities were removed by filtration. The clear solution was concentrated on a water-bath to syrupy consistency and treated with an excess of ethyl alcohol with stirring. Colourless feathery crystals soon began to separate out and the magma was set aside for a day when pure glistening crystals of inositol were obtained. They appeared as broad plates and rods under the microscope, melted at 221–22° and tasted sweet. When mixed with an authentic sample of inactive inositol there was no depression in the melting point and thus its identity was established. Finally the exhausted root powder was further extracted with rectified spirit but no inositol could be obtained from it, its extraction being complete with methyl alcohol. The coloured preliminary extract with methyl alcohol (A) also did not contain any appreciable amount of inositol but they contained saponins and tannins. It was observed that if they were not collected separately at the first stages and removed, inositol could not be obtained in the simple manner described above since the saponins and tannins present kept it in solution and rendered crystallisation very difficult.

The method promises to be capable of wide application in the case of other plant materials. The process of extraction is simple and rapid, the losses in the solvents are negligible and the yield of inositol is quite satisfactory being about 0·4% on the weight of the air-dried roots.

The author's thanks are due to Prof. T. R. Seshadri for his interest in this work.

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MODIFIED REFLECTION OF X-RAYS: NAPHTHALENE

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Received March 15, 1941

1. *Introduction*

The new type of X-ray reflections, recently discovered by Raman and Nilakantan, have attracted the attention of several workers in this field and the subject is now being pursued in various laboratories. We are, at present, engaged in making a detailed study of this phenomenon and some results obtained with calcite have been reported by us earlier in these *Proceedings*.[1] In the course of an attempt to extend the investigations to the region of organic crystals, we have noticed some interesting results in naphthalene and an account of these is given in the present paper.

2. *Experimental Technique*

The source of X-rays is a Shearer tube with a copper anticathode. The incident beam of X-rays, which is carefully collimated by a system of slits, thus contains CuK_α and CuK_β rays along with a certain amount of white radiation. The technique adopted by us for recording the new reflections is similar to the one already described by Raman and Nilakantan[2] in connection with the (111) planes of diamond and by the authors (*loc. cit.*) in connection with the (211) planes of calcite. This technique and the results to be expected therefrom are described here in some detail as it is believed that such a description will clearly bring out the distinction between the normal and the modified X-ray reflections.

A particular set of planes in the crystal is chosen for investigation and by knowing the appropriate spacing, the crystal is set such that these planes are inclined to the incident pencil of X-rays approximately at the correct Bragg angle.* If the reflected spectrum is then recorded, it is clear that one would normally expect to find only a single Laue spot. Such a spot may be attributed to a Bragg reflection from the set of planes under investigation. The reflected beam will consist of CuK_α radiation itself, if the crystal

[1] *Proc. Ind. Acad. Sci.*, 1940, **12**, 337. References to other investigators in this field are contained in our earlier paper.

[2] *Ibid.*, 1940, **11**, 389.

* Correct Bragg angle referred to here relates to CuK_α radiation with $\lambda = 1{\cdot}537$ A.U.

setting is quite accurate. Otherwise, it will consist of either the CuK_β radiation or white radiation of appropriate wave-length lying in the close neighbourhood of the characteristic wave-lengths. The position of this Laue spot will depend very much upon the crystal setting and it will gradually move away from the centre as the crystal is rotated so as to slowly increase the angle of incidence. In addition to this normal type of Bragg reflection, two new spots, which have to be regarded as modified reflections, are usually recorded in this mode of investigation. These two spots come at places where the ordinary Bragg reflections due to CuK_α and CuK_β would appear when the crystal is set suitably for such reflections to take place and they continue to appear at those places or shift only slightly, even when the crystal is tilted considerably away from the critical settings. This behaviour is in marked contradiction to the behaviour of the Bragg reflections. The intensity of the modified spot due to a certain wave-length, say CuK_α, reaches a maximum when the crystal is so oriented that the planes under investigation are also causing CuK_α to be reflected in accordance with the usual Bragg law. It falls off gradually and sometimes rapidly as the crystal is rotated away from this setting. This technique is particularly suited for picking out specific planes, when the crystal structure is known, and studying the modified reflections from them.

3. Results

An organic crystal, namely naphthalene, has been studied in the present investigation. It belongs to the monoclinic prismatic class and crystallises as plates parallel to the (001) plane. This is also a marked cleavage plane and shows an intense Bragg reflection. The spacing is 7·251 A.U. and the corresponding angle of reflection for CuK_α is 6° 5′. The second order reflection by this set of planes (002) occurs at an angle of 12°7′ and is somewhat less intense. Two pictures (Figs. 1 and 2) which have been obtained with this crystal are reproduced in the Plate. The crystal flake is so mounted that the *b*-axis is vertical and that the (001) plane makes about 6° (Fig. 1) and 12° (Fig. 2) with the incident pencil of X-rays. In Fig. 1, the setting is therefore 6° away from the critical setting appropriate to the (002) planes and in Fig. 2, it is similarly 6° away from the critical setting appropriate to the (001) planes. No trace of any modified spot is to be found in the expected place in either case, even though the normal Bragg reflections are recorded very intensely on the axial line. This result is very interesting as it has been the experience of the authors that the modified spots are quite easily recorded at moderately large angles, especially in the inorganic crystals.

With a view to decide whether such reflections are altogether absent in this crystal or are very weak, pictures have been taken in which the

exposures and the resolution are carefully controlled. Figs. 4, 5 and 6 correspond to inclinations of 5°, 6° and 7° respectively of the (001) planes. An aperture of 1·5 mm. diameter has been used in the path of the incident beam with a view to increase the resolution and the exposure time has been cut down with a view to prevent spreading and overlapping. In Figs. 4 and 6, the setting is just one degree different from the proper setting of the (001) planes in respect of the CuK_α radiation and to the left of the intense spot in the former case and to its right in the latter case, may be seen the faint Bragg reflections of appropriate wave-lengths. The intense spot in both these cases is to be regarded as the modified reflection arising from the (001) planes. At larger angles, the modified spot does not appear. If longer exposures are given at smaller angles, the spots are not seen separately because of overlapping due to spreading. Modified reflections from the (002) planes also behave similarly.

Other orientations of the crystal have also been tried but modified spots could not be recorded with appreciable intensity for any of the settings. In the case of the $(20\bar{1})$ plane, which has a large structure factor, a weak modified spot has, however, been recorded at very close angles. This may be seen as a weak spot immediately to the right of the intense Laue spot due to $(\bar{2}01)$, seen on the axial line in Fig. 3.

We have accordingly to conclude that the modified reflections in naphthalene crystals possess appreciable intensity only in the close neighbourhood of the correct Bragg settings. Their intensity falls off very rapidly as the deviation from the Bragg setting increases.

4. *Summary*

Modified X-ray reflections due to (001), (002) and $(20\bar{1})$ planes of naphthalene have been recorded only when the crystal setting is very near that of the critical setting in each case. For orientations which differ appreciably from the above settings, the intensity of the modified spots appears to be very low.

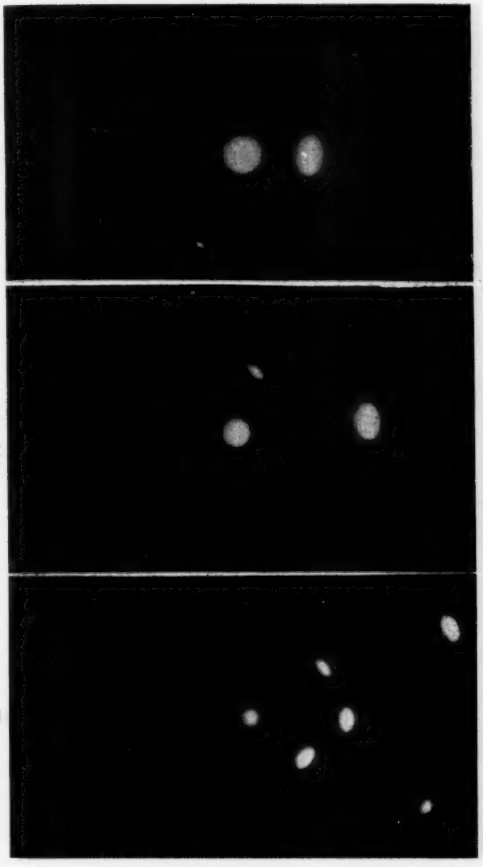

FIG. 1

FIG. 2

FIG. 3

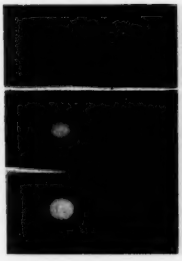

FIG. 4

FIG. 5

FIG. 6

ADAPTATION OF THE MICRO-KJELDAHL METHOD TO THE ESTIMATION OF NITROGEN IN ORGANIC COMPOUNDS CONTAINING NITRO AND AZO GROUPS

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(Communicated by Dr. K. Venkataraman)

Dafert[1] found that the Kjeldahl method of estimation of nitrogen was not applicable to nitro and azo compounds among others without preliminary treatment. It was, therefore, found necessary in the case of such compounds to add a reducing agent at the beginning of the digestion. Jodlbauer[2] suggested the addition of phenol and zinc dust to the digestion mixture. The addition of phenol, resorcinol or phloroglucinol was recommended by Margosches and Scheinost,[3] of zinc by Dafert,[4] of potassium persulphate and zinc dust by Milbauer,[5] of stannous chloride by Kruger[6] and by Flamand and Prager[7] and of sulphur by Eckert.[8] Elek and Sobotka[9] were unable to obtain satisfactory results by these various additions to the digestion mixture for determining nitrogen in nitro and azo compounds by the macro- and micro-methods. Von Asboth[10] estimated nitrogen in nitro and cyano compounds using sugar as a reducing agent. Elek and Sobotka (*loc. cit.*) used glucose as a reducing agent and estimated nitrogen in a number of nitro compounds by modifying the method of Asboth (*loc. cit.*). Using glucose for reduction, Harte[11] analysed a number of nitro and azo compounds by the semi-micro Kjeldahl method. Bradstreet[12] added salicylic acid and sodium thiosulphate to the digestion mixture for effecting the reduction of nitro compounds.

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[1] *Z. anal. Chem.*, 1888, **27**, 224.
[2] *Chem. Centr.*, 1886 (3), **17**, 433.
[3] *Ber.*, 1925, **58**, 1850, 1857.
[4] *Z. anal. Chem.*, 1888, **27**, 222.
[5] *Ibid.*, 1903, **42**, 725.
[6] *Ber.*, 1894, **27**, 1633.
[7] *Ibid.*, 1905, **38**, 559.
[8] *Monatsh.*, 1913, **34**, 1964.
[9] *J. Amer. Chem. Soc.*, 1926, **48**, 501.
[10] *Chem. Centr.*, 1886 (3), **17**, 161.
[11] *Ind. Eng. Chem. Anal. Ed.*, 1935, **7**, 432.
[12] *Ibid.*, 1940, **12**, 657.

While determining nitrogen in azoic dyestuffs on cotton, Forster, Mehta and Venkataraman[13] observed that glucose could be replaced by nitrogen-free cotton in the estimation of nitrogen in azo compounds by the Kjeldahl method. In the present investigation a number of nitro and azo compounds have been found to analyse correctly for nitrogen by the micro-Kjeldahl method, using pure cotton cellulose as reducing agent. The method briefly consists in taking about 0·01 g. of the substance containing about 1–2 mg. nitrogen and adding potassium sulphate, bleached cotton and concentrated sulphuric acid (sp. gr. 1·84). The mixture is heated by a micro-burner. After 30 minutes, copper sulphate and selenious acid are added and the heating continued for some time after the digestion mixture becomes colourless. Ammonia is distilled in a modified form of the Parnas and Wagner's improved micro-Kjeldahl apparatus,[14] and estimated in the usual manner. In the original apparatus the steam generator is connected to the side-tube, *l*, of the cylindrical receiver, the top of which is closed by a stopper, *k*. Through this stopper passes a glass tubing connecting the cylindrical receiver with the distilling flask. According to Pregl (*loc. cit.*) the burner under the steam generator is removed after the distillation of ammonia is over; the removal of the burner causes a drop of pressure in the steam generator, as a result of which the whole of the contents of the distilling flask are sucked back into the cylindrical receiver. It was observed during the present investigation that the alkaline liquor that is sucked back into the cylindrical receiver tends to go through the side tube, *l*, into the steam generator. This is eliminated if the steam generator is connected to the cylindrical receiver at *k* and the distilling flask to the side tube, *l*, of the cylindrical receiver.

This method is very useful in estimating dyestuffs on the fibre, and hence in grading dyeings with reference to their fastness to rubbing. It can be utilised also for grading dyeings with reference to their fastness to kier boiling and light, provided no chemical changes take place in the dyestuff molecules during these operations.

Experimental

About 0·01 g. of the substance was weighed on a piece of filter-paper weighing about 0·05–0·08 g., the filter-paper folded and introduced into a dry Kjeldahl flask. About 1–1·5 g. potassium sulphate, 0·3–0·5 g. bleached nitrogen-free cotton and 4 c.c. concentrated sulphuric acid were next added. The flask was supported in a slanting position and heated by

[13] *J. Soc. Dyers Col.*, 1938, **54**, 210.

[14] *Quantitative Organic Micro-analysis*, by F. Pregl, translated by E. Fyleman, Second Ed., 1930, Fig. 22, p. 109.

a micro-burner. After half an hour, 20–30 mg. copper sulphate and about 20 mg. selenious acid were added, the sides of the flask washed with 1 c.c. sulphuric acid and heating continued. The mixture became a clear, green solution in the course of an hour. The heating was continued for 15–20 minutes longer. On cooling, 2–3 c.c. distilled water were added and the mixture allowed to cool after thorough shaking. The distillation was carried out in the Pregl apparatus. The digested mixture was poured into the distilling flask of the apparatus through the funnel, the digestion flask well washed, 25 c.c. of 50% caustic soda solution containing 8% sodium thiosulphate added and the distillation conducted in the usual way. The ammonia was received in a beaker containing 25 c.c. of 0·01 N hydrochloric acid to which about 0·3–0·4 c.c. of the indicator[15] was added. The indicator was prepared by mixing 2 c.c. of 1% aqueous methylene blue solution with 100 c.c. of 0·04% solution of methyl red in 50% alcohol. After distilling for 6 minutes the beaker containing the acid was lowered, distillation continued for 1 minute more, the end of the silver condenser washed into the beaker and the acid back titrated with 0·01 N sodium hydroxide. The change of colour from pink to green showed the end-point, which was quite sharp. The blank values on the reagents varied from 0·3 c.c. to 0·4 c.c. of 0·01 N sodium hydroxide.

The following are some representative results:

Compound	Molecular formula	% N calculated	% N found
1. *p*-Nitraniline	$C_6H_6O_2N_2$	20·29	20·32, 20·30
2. *p*-Aminoazobenzene	$C_{12}H_{11}N_3$	21·31	21·32, 20·99
3. 3:5-Dinitrobenzoic acid	$C_7H_4O_6N_2$	13·21	13·29, 13·32
4. Fast Bordeaux Base GP (3-Nitro-4-aminoanisole)	$C_7H_8O_3N_2$	16·66	16·69, 16·70
5. Cinnamoyl-*p*-nitranilide	$C_{15}H_{22}O_3N_2$	10·69	10·45, 10·49
6. *p*-Toluene sulphonyl-*p*-nitranilide ..	$C_{13}H_{12}O_4N_2S$	9·59	9·86, 9·72
7. 2:4-Dinitrophenyl hydrazone of 2-methoxy-3-naphthaldehyde ..	$C_{18}H_{14}O_5N_4$	15·30	15·20
8. 2:4-Dinitrophenyl hydrazone of 2-methoxy-3-acetonaphthone ..	$C_{19}H_{16}O_5N_4$	14·73	14·50
9. Azo dye from naphtol AS-SW (2-hydroxy-3-naphthoyl-β-naphthalide) and diazotised Fast Bordeaux Base GP (3-nitro-4-aminoanisole) ..	$C_{28}H_{20}O_5N_4$	11·39	11·18, 11·59

[15] Andersen and Jensen, *Z. anal. Chem.*, 1931, **83**, 114.

Compound	Molecular formula	% N calculated	% N found
10. Azo dye from naphtol AS-D (2-hydroxy-3-naphthoyl-*o*-toluidide) and diazotised Fast Red Base GL (3-nitro-4-aminotoluene)	$C_{25}H_{20}O_4N_4$	12·73	12·66, 12·58
11. Azo dye from naphtol AS (2-hydroxy-3-naphthanilide) and diazotised Fast Red Base B (5-nitro-2-aminoanisole)	$C_{24}H_{18}O_5N_4$	12·67	12·68, 12·64
12. Azo dye from naphtol AS-BS (2-hydroxy-3-naphthoyl-*m*-nitranilide) and diazotised Fast Red Base GL (3-nitro-4-aminotoluene)	$C_{24}H_{17}O_6N_5$	14·86	14·57, 14·61
13. Azo dye from naphtol AS-SW (2-hydroxy-3-naphthoyl-β-naphthalide) and diazotised Fast Red Base B (5-nitro-2-aminoanisole)	$C_{28}H_{20}O_5N_4$	11·39	11·33, 11·57
14. Azo dye from naphtol AS (2-hydroxy-3-naphthanilide) and diazotised Fast Blue Base BB (4-benzoylamido-2: 5-diethoxyaniline)	$C_{34}H_{30}N_4O_5$	9·76	9·72, 9·50
15. Azo dye from naphtol AS (2-hydroxy-3-naphthanilide) and diazotised Fast Red Base RBE (4-amino-6-benzoylamido-1 : 3-xylene)	$C_{32}H_{26}N_4O_3$	10·89	10·80, 10·83
16. Azo dye from naphtol AS (2-hydroxy-3-naphthanilide) and diazotised Fast Red Base GL (3-nitro-4-aminotoluene)	$C_{24}H_{18}O_4N_4$	13·14	13·13, 13·24
17. Azo dye from β-naphtol and diazotised Fast Yellow Base GC (*o*-chloroaniline)	$C_{16}H_{11}ON_2Cl$	9·91	9·67, 9·70
18. Azo dye from naphtol AS (2-hydroxy-3-naphthanilide) and diazotised Fast Scarlet Base GG (2: 5-dichloraniline)	$C_{23}H_{15}O_2N_3Cl_2$	9·63	9·34, 9·32

Thanks are given to Dr. K. Venkataraman for his interest in the work.

STUDIES IN CHLORAL AMIDES

Part VII. Reactivity of the α-OH Group in Chloral Bromo Salicylamides and Their Methyl Ethers

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(Communicated by Dr. Mata Prasad, D.Sc., F.A.Sc.)

In continuation of the work on bromo chloral salicylamides[1] the reactivity of α-OH group in chloral 3-bromo salicylamide, chloral 5-bromo salicylamide, chloral 5-bromo 2-methoxy benzamide, chloral 3 : 5-dibromo salicylamide and chloral 3 : 5-dibromo 2-methoxy benzamide has further been studied on lines described in a previous paper.[2]

The action of acetic anhydride in the alkaline medium gave anhydro compound (*cf.* Ref. 2); while the acidic medium gave completely acetylated products.

Benzoyl chloride as expected gave the simple benzoyl derivatives; while dimethyl sulphate gave completely methylated compounds.

The yields are more or less quantitative throughout.

Experimental

The methods used for the preparation of various derivatives were the same as used previously (*cf.* Ref. 2).

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[1] Hirwe, Patil and (Miss) Gavankar, *Proc. Ind. Acad. Sci.* (A), 1940, **11**, 512.
[2] Hirwe and (Miss) Gavankar, *J. Univ. Bombay*, 1937, **6**, Part II, 123.

Compound	Solvent	Crystalline nature	M.P.	Molecular formula	Found percent	Required percent
Chloral 3-bromo-α-2-diacetoxy benzamide ..	alcohol	clusters of needles	119–20°	$C_{13}H_{11}O_5NCl_3Br$	halogen 42·0	41·7
Chloral 5-bromo-α-2-diacetoxy benzamide ..	,,	needles	151–52°	$C_{13}H_{11}O_5NCl_3Br$	halogen 41·9	41·7
Chloral 5-bromo-α-acetoxy-2-methoxy benzamide	,,	,,	134–35°	$C_{12}H_{11}O_4NCl_3Br$	halogen 44·4 N 29·0	44·5 3·3
Chloral 5-bromo-α-2-dibenzoyloxy benzamide ..	methyl alcohol	plates	97–100°	$C_{23}H_{15}O_3NCl_3Br$	halogen 33·2	32·6
Chloral 5-bromo-α-benzoyloxy-2-methoxy benzamide	alcohol	prisms	145–46°	$C_{17}H_{13}O_4NCl_3Br$	halogen 38·0 N 3·0	38·7 2·9
Chloral 5-bromo-α-2-dimethoxy benzamide ..	,,	cubes	160 °	$C_{11}H_{11}O_3NCl_3Br$	halogen 47·9 N 3·5	47·8 3·6
Anhydro (5-bromo-2-methoxy chloral benzamide)	,,	,,	149–50°	$C_{20}H_{16}O_5N_2Cl_6Br_2$	halogen 50·4	50·6
Chloral 3 : 5-dibromo-α-2-diacetoxy benzamide	,,	needles	155–57°	$C_{13}H_{10}O_5NCl_3Br_2$	halogen 51·1 N 2·6	50·6 2·7
Chloral 3 : 5-dibromo-α-acetoxy-2-methoxy benzamide	,,	,,	117–19°	$C_{12}H_{10}O_4NCl_3Br_2$	halogen 52·8	53·3
Chloral 3 : 5-dibromo-α-benzoyloxy-2-methoxy benzamide	acetone	plates	124–26°	$C_{17}H_{12}O_4NCl_3Br_2$	halogen 46·7	47·5
Chloral 3 : 5-dibromo-α-2-dimethoxy benzamide	alcohol	rhomboids	108–09°	$C_{11}H_{10}O_3NCl_3Br_2$	halogen 56·9 N 3·0	56·6 3·0
Chloral 3 : 5-dibromo-α-methoxy-2-hydroxy benzamide	,,	parallelo epipodes	176–77°	$C_{10}H_8O_3NCl_3Br_2$	halogen 58·9 N 3·1	58·4 3·1
α-Anhydro-(3 : 5-dibromo-2-methoxy chloral benzamide)	,,	cubes	136–37°	$C_{20}H_{14}O_5N_2Cl_6Br_4$	halogen 59·8	59·7

Acknowledgment of thanks is due to (Miss.) K. D. Gavankar who has written up the paper for publication from the M.Sc. thesis of one of the authors.

STUDIES IN CHLORAL AMIDES

Part VIII. Condensation of Toluic Amides with Chloral

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The condensation of chloral with the amides of *o*-, *m*-, and *p*-toluic acids has been studied in this paper. The condensation proceeds readily in all the cases with the formation of the corresponding chloral amides.

In acetylation and methylation the results obtained are of the same kind as referred to before,[1] except that in acetylation, besides the usual anhydro derivative small quantities of acetyl derivatives are also found. Benzoylation of *o*-toluic amide in the presence of alkali gives the normal benzoyl derivative together with the anhydro compound. In the cases of *m*- and *p*-toluic amides, the benzoylation in the presence of alkali affords in each case two compounds one of which is the anhydride identical with that obtained by the action of acetic anhydride in the presence of alkali; the nature of the other compound is under investigation.

Experimental

The methods used for the preparation of the amide, chloral amides and their various derivatives, were the same as used by the previous workers.

Chloral-o-toluic-amide.—Crystallised from alcohol in rhombic plates, m.p. 151–53°. (Found: Cl, 37·4; N, 4·8; $C_{10}H_{10}O_2NCl_3$ requires Cl, 37·7; N, 4·9 per cent.)

α-Methoxy-chloral-o-toluic-amide.—Crystallised from alcohol in needles, m.p. 120–21°. (Found: Cl, 35·7; $C_{11}H_{12}O_2NCl_3$ requires Cl, 35·9 per cent.)

α-Acetoxy-chloral-o-toluic-amide.—This compound obtained by two methods: (1) By the action of acetic anhydride with a few drops of sulphuric acid and (2) by the action of acetic anhydride in an alkaline medium crystallised from alcohol in needles, m.p. 159–60°. (Found: Cl, 33·0; $C_{12}H_{12}O_3NCl_3$ requires Cl, 32·8 per cent.)

α-Benzoyl-chloral-o-toluic amide.—Obtained by the direct action of benzoyl chloride on the condensation product and also by the action of benzoyl chloride in an alkaline medium, crystallised from alcohol, m.p. 149–51°. (Found: Cl, 27·9; $C_{17}H_{14}O_3NCl_3$ requires Cl, 27·5 per cent.)

From the M.Sc. thesis of one of the authors.

The second product which is the anhydro compound and obtained from the above alcoholic mother liquor, crystallised from glacial acetic acid in needles, m.p. 219–20°. (Found: Cl, 38·8; $C_{20}H_{18}O_3N_2Cl_6$ requires Cl, 38·9 per cent.)

This compound could also be obtained by the action of acetic anhydride on the chloral *o*-toluic amide in an alkaline medium—mixed m.p. with the above was 219–20°.

Chloral-m-toluic-amide.—Crystallised from alcohol in rhobmic plates, m.p. 145°. (Found: Cl, 38·0; $C_{10}H_{10}O_2NCl_3$ requires Cl, 37·7 per cent.)

α-Acetoxy-chloral-m-toluic-amide.—Prepared by acetic anhydride sulphuric acid method was crystallised from alcohol in needles, m.p. 142°. (Found: Cl, 32·5; $C_{12}H_{12}O_3NCl_3$ requires Cl, 32·8 per cent.)

α-Benzoyloxy-chloral-m-toluic amide.—By the action of benzoyl chloride on the chloral-*m*-toluic-amide. It crystallised from alcohol in needles, m.p. 157–58°. (Found: Cl, 27·2·; $C_{17}H_{14}O_3NCl_3$ requires Cl, 27·5 per cent.) Action of benzoyl chloride on chloral-*m*-toluic-amide in an alkaline medium gave a mixture from which anhydro compound was separated and crystallised from acetone, m.p. 165–67°. (Found: Cl, 39·0; $C_{20}H_{18}O_3N_2Cl_6$ requires Cl, 38·9 per cent.)

The mother liquor on concentration afforded the other product which crystallised from alcohol in needles, m.p. 150–52°. (Found: Cl, 40·3; $C_{20}H_{16}O_2N_2Cl_6$ requires Cl, 40·3 per cent.)

Chloral-p-toluic amide.—Crystallised from alcohol in hexagones, m.p. 151–52°.

α-Acetoxy-chloral-p-toluic-amide.—By the action of acetic anhydride and sulphuric acid on chloral *p*-toluic amide. It crystallised from methyl alcohol in needles, m.p. 159–60°. (Found: Cl, 32·6; $C_{12}H_{12}O_3NCl_3$ requires Cl, 32·8 per cent.)

Action of benzoyl chloride on chloral *p*-toluic amide in an alkaline medium gave a product which on crystallisation from dilute alcohol gave anhydro chloral *p*-toluic amide, m.p. 200°-02°. (Found: Cl, 39·2; $C_{20}H_{18}O_3N_2Cl_6$ requires Cl, 38·9 per cent.)

The second crop crystallised from acetone in needles, m.p. 198–200°. (Found: Cl, 40·0; $C_{20}H_{16}O_2N_2Cl_6$ requires Cl, 40·3 per cent.)

Acknowledgment of thanks is due to (Miss) K. D. Gavankar, who has written up the paper for publication from the M.Sc. thesis of one of the authors.

STUDIES IN CHLORAL AMIDES

Part IX. Reactivity of α-Chlorine in α-Chloro-chloral-toluic Amides

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As expected,[1] α-chloro-chloral toluic amides are found to possess reactive α-chlorine atom which has been proved by reaction with various reagents such as alcohols, phenols, primary and secondary amines.

Potassium cyanide (1 mol.) reacts very rapidly with the α-chloro compound (I) but the pure α-cyano compound cannot be isolated. With potassium cyanide (2 mols.) a product is isolated which is not the expected α-cyano compound but which appears to have the unsaturated structure III and whose formation may be explained as follows:

$$\underset{\text{I}}{R\cdot CO\cdot NHCH(Cl)CCl_3} \xrightarrow{KCN} \underset{\text{II}}{R\cdot CONH\cdot CH(CN)CCl_3} \xrightarrow{KCN} \underset{\text{III}}{R\cdot CO\cdot NH\cdot C(CN):CCl_2}$$

Hirwe and Rana[2] have obtained analogous results with α-chloro-chloral-chloro-2-methoxy and α-chloral-chloro-bromo-2-methoxy benzamide and potassium cyanide.

The production of such an unsaturated compound in the presence of an alkali has been previously observed by Goldschmitt[3] who found that $CH(C_6H_4Br)_2CCl_3$ gives an unsaturated compound $(C_6H_4Br)_2C:Cl_2$.

The nitrites have been further hydrolysed by means of hydrochloric acid to the corresponding acids of the type—$R\cdot CO\cdot NHC(COOH):C:Cl_2$.

Experimental

General Methods.—

Preparation of α-chloro-chloral toluic amides.—A mixture of finely powdered chloral-toluic amide (5 g.) and phosphorous pentachloride (5 g.) was heated on a water-bath with a calcium chloride tube for two hours when

[1] Feist with Nissan and Stadler Br., 1914, 47, 1173.
[2] *J. Ind. Chem. Soc.*, 1940, 8, 481.
[3] *Ber.*, 6, 985, 99.

Compound	Solvent	Crystalline nature	M.P.	Molecular formulæ	Found %		Required %
α-Chloro-chloral-*o*-toluic amide	acetone	needles	172–73°	$C_{10}H_9ONCl_4$	Cl	46·8	47·2
α-Methoxy chloral-*o*-toluic amide	methyl alcohol	plates	121°	$C_{11}H_{12}O_2NCl_3$	Cl	35·7	35·9
α-Ethoxy chloral-*o*-toluic amide	alcohol	needles	127–28°	$C_{12}H_{14}O_2NCl_3$	Cl	34·5	34·3
α-Amino chloral-*o*-toluic amide	acetone alcohol	,,	228–29°	$C_{10}H_{11}ON_2Cl_3$	Cl	37·9	37·8
α-Aniline chloral-*o*-toluic amide	alcohol	,,	176–77°	$C_{16}H_{15}ON_2Cl_3$	Cl	30·0	29·8
α-Methyl anilino chloral-*o*-toluic amide ..	,,	,,	135–36°	$C_{17}H_{17}ON_2Cl_3$	Cl	28·6	28·7
α-Phenoxy chloral-*o*-toluic amide	,,	,,	146–47°	$C_{16}H_{14}O_2NCl_3$	Cl	29·6	29·7
α-Chloro-chloral-*m*-toluic amide	benzene	,,	132–34°	$C_{10}H_9ONCl_4$	Cl	47·0	47·2
α-Methoxy chloral-*m*-toluic amide	methyl alcohol	rhombic plates	98°	$C_{11}H_{12}O_2NCl_3$	Cl	35·7	35·9
α-Ethoxy chloral-*m*-toluic amide	alcohol	needles	145–46°	$C_{12}H_{14}O_2NCl_3$	Cl	34·4	34·3
α-Amino chloral-*m*-toluic amide	,,	plates	208–10°	$C_{10}H_{11}ON_2Cl_3$	Cl	37·8	37·8
α-Anilino chloral-*m*-toluic amide	,,	needles	166 °	$C_{16}H_{15}ON_2Cl_3$	Cl	29·8	29·8
α-*o*-Anisidino chloral-*m*-toluic amide	methyl alcohol	,,	149°	$C_{17}H_{17}O_2N_2Cl_3$	Cl	27·6	27·5
α-*o*-Phenetidino chloral-*m*-toluic amide ..	,,	plates	145°	$C_{18}H_{19}O_2N_2Cl_3$	Cl	26·6	26·5
α-Phenoxy chloral-*m*-toluic amide	alcohol	silky needles	140–41°	$C_{16}H_{14}O_2NCl_3$	Cl	29·4	29·7
α-*o*-Crisoloxy-chloral-*m*-toluic amide	,,	needles	156°	$C_{17}H_{16}O_2NCl_3$	Cl	28·4	28·6

β-Dichloro-α-cyanovinyl-*m*-methyl benzamide ..	,,	plates	161°	$C_{11}H_8ON_2Cl_2$	Cl N C H	27·9 11·2 52·2 2·5	27·8 11·1 52·0 2·8
β-Dichloro-α-carboxy vinyl-*m*-methylbenzamide	,,	needles	189°	$C_{11}H_9O_3NCl_2$	Cl equiva- lent	25·9 272·4	25·9 27·4
α-Chloro-chloral-*p*-toluic amide	benzene	,,	111°	$C_{10}H_9ONCl_4$	Cl	47·0	47·3
α-Methoxy chloral-*p*-toluic amide	methyl alcohol	rectangular plates	112–13°	$C_{11}H_{12}O_2NCl_3$	Cl	36·1	35·9
α-Ethoxy chloral-*p*-toluic amide	alcohol	plates	116–17°	$C_{12}H_{14}O_2NCl_3$	Cl	34·3	34·3
α-Amino chloral-*p*-toluic amide	methyl alcohol	,,	210°	$C_{10}H_{11}ON_2Cl_3$	Cl	37·7	37·8
α-Aniline chloral-*p*-toluic amide	alcohol	needles	132°	$C_{16}H_{15}ON_2Cl_3$	Cl	29·6	29·8
α-*o*-toluidino chloral-*p*-toluic amide	methyl alcohol	,,	153°	$C_{17}H_{17}ON_2Cl_3$	Cl	28·6	28·7
α-Piperidino chloral-*p*-toluic amide	alcohol	,,	132°	$C_{15}H_{19}ON_2Cl_3$	Cl	30·7	30·5
α-Phenoxy chloral-*p*-toluic amide	,,	,,	129–31°	$C_{16}H_{14}O_2NCl_3$	Cl	29·4	29·7
β-Dichloro-α-cyano vinyl-*p*-methyl benzamide ..	,,	rectangular plates	167°	$C_{11}H_6ON_2Cl_2$	Cl	28·0	27·8
β-Dichloro-α-carboxy vinyl-*p*-methyl benzamide	,,	needles	180°	$C_{11}H_9O_3NCl_2$	Cl equiva- lent	25·8 274·8	25·9 274
Sodium salt	water	,,	..	$C_{11}H_8O_3NCl_2Na$, $2\,H_2O$	Na H_2O	7·1 11·0	6·9 10·8
Barium salt	,,	,,	..	$C_{22}H_{16}O_6N_2Cl_4Ba$ H_2O	Ba	19·6	19·5

the whole mixture liquefied. After cooling it was poured on to crushed ice when the α-chloro compound separated.

The α-amino compounds—were prepared by the action of ammonium carbonate on the α-chloro compounds.

Potassium cyanide reaction.—The method used is the same as used by previous workers (*cf.* Ref. No. 2).

Acknowledgment of thanks is due to (Miss) K. D. Gavankar, who has written up the paper for publication from the M.Sc. thesis of one of the authors.

DISPERSION OF ULTRASONIC VELOCITY IN ORGANIC LIQUIDS

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1. *Introduction*

In an earlier communication[1] it was shown that there was no definite evidence of acoustic dispersion in Benzene, Carbon-tetrachloride, Water, Carbon-disulphide and Xylol. Recently, E. C. Richardson[2] using a hot-wire detector and frequencies between 200 kc and 1110 kc found no dispersion of acoustic velocity in these liquids.

The present paper contains the results of new work in which seventeen organic liquids have been examined using the diffraction method and frequencies ranging from 3000 kc to 8000 kc.

2. *Experimental*

The experimental arrangement used in previous work was employed both for the production of the ultrasonic waves and for photographing the resulting diffraction spectra.

In addition to the two quartz crystals used in the earlier work a third one was also employed to give about 3·5 mc, 4·0 mc, 8·0 mc and in some cases 22·0 mc.

Very rapid photographic plates and a strong source of light were used. The frequencies were measured by a precision wavemeter made by the General Radio Co. The temperature was taken just at the time of taking the diffraction spectra and each liquid was thoroughly stirred before taking the temperature. The purest available liquids were distilled carefully before using.

3. *Results*

Very sharp diffraction fringes were obtained and the distances between the fringes were measured on a Hilger Comparator. The wavelength of light used was 5461 Å obtained from a mercury arc. The results were calculated by using the usual formula for the diffraction method and are tabulated in Table I.

TABLE I

Dispersion of Ultrasonic Velocity

Liquid	Temperature in °C.	Frequency in Kc	Velocity in metres per sec.
1. Amyl acetate	29·6	3607 4089 7933	1179 1179 1179
2. Butyl acetate	29·2	3527 7925	1178 1176
3. Ethyl acetate	29·3	3522 4092 7799	1130 1129 1128
4. Methyl acetate	29·4	3687 4114 7933	1144 1143 1142
5. Propyl acetate	29·3	3532 4258 8013	1147 1148 1147
6. Amyl formate	29·0	3527 4114 7831	1188 1187 1188
7. Ethylene dichloride	27·1	3501 4101 8209	1185 1183 1184
8. Acetone	27·3	3483 4038 22335	1166 1167 1168
9. Ethyl chloro-acetate	29·3	1543 3693 4051 22320	1253 1253 1252 1253
10. Picoline	30·5	4114 7000	1298 1297
11. Chloro-benzene	27·8	3513 4304 7869	1248 1247 1248
12. Propyl alcohol	27·8	3493 4070 22447	1203 1201 1204
13. Hexane	28·2	3614 4214 7846	1080 1081 1082
14. Chloroform	26·8	3503 4127 7996	978·3 978·1 977·9

TABLE I—*Contd.*

Liquid	Temperature in °C.	Frequency in Kc	Velocity in metres per sec.
15. Ethyl ether	25·5	3613 4135 7981	971·8 969·6 972·9
16. Methyl iodide	25·8	3507 4108 8079	832·6 830·3 832·8
17. Acetic acid	26·0	3560 4234 7618	1131 1136 1144

4. *Discussion*

It may be of significance that of the seventeen substances examined only acetic acid appears to show a systematic variation with wavelength although this variation is very small and rather near the limits of experimental error. It may be pointed out that Spakovskij[3] has observed an increase in velocity of 1% between frequencies 200 kc and 3000 kc for acetic acid.

The author wishes to thank Professor J. West, D.SC., F.INST.P., for his kind encouragement.

5. *Summary*

Ultrasonic velocities have been determined for seventeen organic liquids employing three ranges of frequencies between 3500 kc and 8000 kc. In the case of Ethyl chloro-acetate, Acetone and Propyl alcohol an additional frequency of about 22300 kc was used. With the exception perhaps of acetic acid, there appears to be no evidence of dispersion in any of the liquids within the range of frequencies employed.

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3. Spakovskij, B. .. *C. R.* (*U.S.S.R.*), 1938, **18**, 169.

TEMPERATURE VARIATION OF THE RAMAN FREQUENCY OF DIAMOND

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Received April 5, 1941

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The Raman spectrum of diamond has been studied by Ramaswamy (1930), Bhagavantam (1930) and Robertson, Fox and Martin (1930), and found to consist of a strong line of frequency 1332 cm.$^{-1}$ Ramaswamy found that the line was unaffected by heating the crystal to 250° and Robertson *et al.* also obtained a similar result on cooling to −180°. It is doubtful however, whether the measurements were carried out with sufficient accuracy to detect small changes of frequency, as we should expect to find some change in the frequency however small it might be, with the expansion of the lattice. It is known that in the case of quartz, the Raman lines are notably affected by temperature, and recent investigations indicate that striking changes occur in the case of lines which represent modes of oscillations of the atoms leading to a polymorphic transition of the crystal (Raman and Nedungadi, 1940; Saxena, 1940). Numerous investigators have found that diamond undergoes a transformation at about 1800° and becomes graphite. The transition temperature has been derived theoretically by Nagendra Nath (1934) on the basis of the dynamics of the oscillation of the diamond lattice. According to this author, the 1332 line has its origin in the oscillation of the two interpenetrating cubic lattices forming the diamond structure against each other, and the increasing amplitude of the vibration with temperature, at a certain stage brings about the transformation from the cubic to the hexagonal form. The thermal behaviour of the Raman line is therefore of interest and in the present investigation the change of the Raman frequency has been studied over a wide range of temperatures.

2. Experimental

(i) *Room temperature.*—The 1332 line of diamond is very intense and can be recorded with even a small crystal. A specially suitable crystal roughly octahedral in shape and practically free from fluorescence was

employed to get some intense pictures. The line could be recorded with moderate intensity with barely an hour's exposure, but even as much as 120 times this exposure failed to bring out any other lines. The 6 other faint lines reported by Bhagavantam are therefore of extremely small intensity and probably secondary in origin. The mean value at room temperature (25°) from 8 plates taken during the course of these investigations gave the value 1332·1, closely agreeing with the values 1331·9 given by Bhagavantam and 1332·2 given by Robertson *et al.*

(ii) *High temperatures.*—In the investigation already referred to, Ramaswamy used the simple device of embedding the crystal in a copper bar and keeping it hot by an electric heater. The present investigation aimed at studying the scattered spectrum up to the highest practicable temperatures and a more elaborate experimental arrangement was found necessary. Robertson (1936) found that heating in air at about 700° causes the surfaces of the crystals to be tarnished. Actually it has been found that prolonged heating at even 400° brings about this effect so that it was necessary to heat the crystal in an inert atmosphere.

The experimental arrangement is illustrated in Fig. 1 *a*. The crystal was held in a small porcelain tube open at both ends, wound with nichrome wire, and was supported in the centre of a pyrex glass bulb by a long porcelain stem. The bulb was sealed at the bottom and was kept filled with nitrogen at a low pressure after it had been evacuated and washed out with this inert gas a number of times. A calibrated iron-constantan thermo-junction was held in contact with the diamond and the actual temperature reached was measured by means of a Weston millivoltmeter. The efficient thermal insulation provided for the heating element and crystal made it possible for temperatures up to 1000° to be easily obtained.

The light from a mercury pointolite lamp was condensed on the crystal in a backward direction and the scattered light was caught by the spectrograph. The instrument used was a Fuess spectrograph with dispersion about 20 Å mm. in the 4358 region. Four exposures were made at intervals of about 250° C. side by side using a Hartmann diaphragm. The progressive lowering of frequency can be seen in the pictures of the Raman spectra reproduced in Plate XIV. The crystal remained undamaged up to 830° C. but at a higher temperature, the surface rapidly assumed a frosted appearance. This factor and the light due to the thermal glow of the diamond made it impossible to carry on the studies to higher temperatures. Two additional pictures were obtained at 180° and 240° to get a smooth curve.

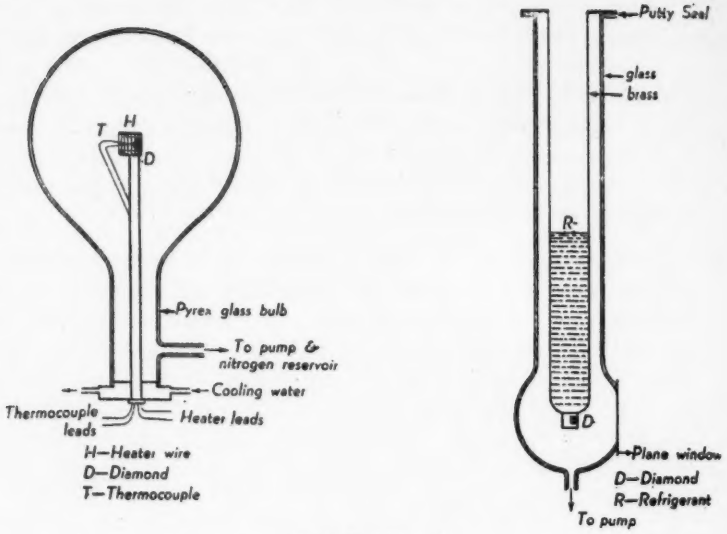

FIG. 1 *a* and 1 *b*

Apparatus for study of scattering at (*a*) High Temperatures, (*b*) Low Temperatures

(iii) *Low temperatures.*—Since the crystal was of very small size, the usual method of immersion in liquid air or other cooling agent was found to be unsuitable. For the low temperature work therefore, a demountable vacuum flask with the inner vessel of metal and outer vessel of glass was employed (Fig. 1 *b*). The lower portion of this vessel was made into a bulb with a flat window for observation of the scattered light. The diamond was held in a copper block fixed to the bottom of the thin-walled brass cylinder which contained the refrigerant. The flanged joint between the metal and glass parts at the top was sealed with Metro-Vick Putty, and the vacuum was maintained by an oil diffusion pump. The performance of this arrangement was very satisfactory requiring refilling with liquid air only once in about two hours. Two low temperature measurements were obtained by using liquid air in one case and solid CO_2-acetone mixture in the other case. Since the change in frequency is small at low temperatures, at least two independent determinations were made in each case. The plates were measured with a Hilger cross-slide micrometer reading up to 1/1000 mm.

3. *Results*

The frequencies at different temperatures are given in Table I, and illustrated in the curve in Fig. 2.

TABLE I

Frequencies of Raman line of Diamond at different temperatures

Absolute temperature	Frequency cm.$^{-1}$	Remarks
85	1333·8	Liquid air cooling. Mean of two plates
195	1333·0	Solid CO_2-acetone
300	1332·1	Mean of 8 plates
455	1331·0	..
515	1329·3	Two plates
595	1327·9	do.
905	1321·9	..
1130	1316·4	..

It can be seen readily from the curve that at low temperatures, the change of frequency is small which explains the negative results obtained by earlier workers. The diminution in frequency from liquid air to room temperatures is small compared with that corresponding to a similar interval above room temperature. At still higher temperatures, the change of frequency is more rapid. The line remains sensibly sharp throughout, but at the highest temperature studied, a tendency to become diffuse is just noticeable. This point could not be followed up further as the light due to the glow of the diamond prevents a satisfactory spectrum being obtained.

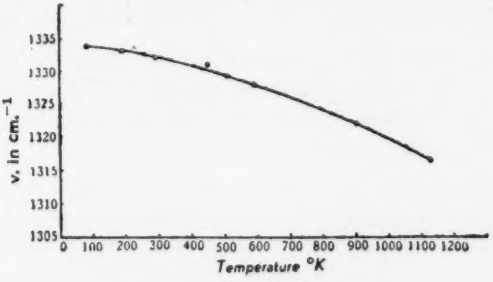

FIG. 2

Frequency-Temp. Curve of Diamond

4. Discussion

(i) *The nature of the oscillation.*—The structure of diamond was shown by Bragg to consist of two cubic lattices interpenetrating each other so that

every atom of one lattice is surrounded tetrahedrally by four atoms of the other lattice. As has been indicated briefly before, Nagendra Nath considered the oscillation of the two lattices against each other and derived a single frequency of the correct magnitude active in Raman effect and absent in the infra-red. Identical results have been obtained by Venkatarayudu (1939) by the use of the group-theoretical method. That this picture is correct is borne out by the experimental fact that the Raman spectrum is a single line of exceptional intensity which is inactive in the infra-red. The lines of very low intensity observed by Bhagavantam and the infra-red frequencies found by Robertson and others are possibly to be ascribed to departure from perfection of the crystals. The point of special interest regarding the 1332 line is that it is a lattice oscillation of frequency much higher than what is generally met with in other crystals. The thermal behaviour of the line is also in agreement with this fact.

(ii) *Change of frequency in relation to thermal expansion.*—Since the vibration of the lattice is a single (triply degenerate) oscillation, the relationship between the pressure, volume and temperature may be based on the simple Einstein model. From the general equation of state for a solid, the relation between thermal and elastic constants and the frequency has been derived by Gruneisen in the form

$$\frac{\alpha V_0}{\chi_0 C_v} = -\frac{d(\log \nu)}{d(\log V)},$$

where α is the thermal expansion coefficient, V_0 is the volume of a gram atom of the solid, χ_0 is the compressibility at zero degrees, C_v is the atomic specific heat and ν the frequency.

The value of the constant $\frac{d(\log \nu)}{d(\log V)}$ denoted by γ has not been directly determined theoretically or experimentally, but from the known values of α, V_0, χ_0 and C_v the values have been calculated for a number of crystals (Gruneisen, *Handb. der Physik*, **10**, p. 28). The relevant constants for diamond are taken from the table given by Gruneisen.

TABLE II

Thermo-elastic properties of diamond (20° C.)

Atomic weight	Density	Atomic vol. V_0	Expansion coefficient $\frac{1}{V}\cdot\frac{dV}{dt}\cdot 10^6$ α	Compressibility $-\frac{1}{V}\cdot\frac{dV}{dP}\cdot 10^{12}$ χ	Atomic heat $C_v \cdot 10^{-7}$	$\gamma = \frac{\alpha V_0}{\chi_0 C_v}$
12·0	3·51	3·42	2·91	0·16	5·66	1·10

An estimate of the change of frequency with volume can be made from this relation (Mott and Jones, 1936) but the reverse process of calculating the thermal expansion from a knowledge of the characteristic frequency at different temperatures has not been carried out before. Diamond offers a favourable case where an attempt in this direction can be made with the Raman spectrum data. Since the energy and frequency are functions of the volume, the relation can be changed into the form

$$\alpha^2 = \frac{\chi_0 C_v}{V} \cdot \frac{1}{\nu} \cdot \frac{d\nu}{dT}.$$

From the value of $\frac{d\nu}{dT}$ derived from the above experimental values, the thermal expansion coefficient has been calculated for different temperatures. In the formula given earlier, χ_0 is strictly the compressibility at zero degrees, but the available experimental value at 20° is used, as the difference will be very little for a crystal of extremely low compressibility like diamond. The values of C_v are interpolations from the values of Nernst, Lindeman and Weber.

The experimental values of α for different temperatures are derived from the linear expansion coefficients quoted by Gruneisen (*loc. cit.*). These are represented in a curve in Fig. 3 along with the values calculated from

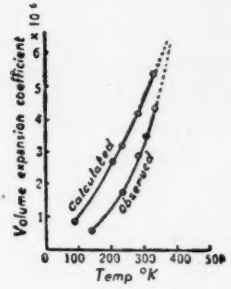

FIG. 3

Thermal expansion coefficient observed and calculated values

the experimental data. It can be seen at once that the figures obtained from these calculations are of the right order but considerably higher than the actual values. At 20° C., the value calculated from the present experiments is $4{\cdot}5 \times 10^{-6}$ while the actual value is $2{\cdot}9 \times 10^{-6}$. Proceeding the other way, we can also calculate the change of frequency to be expected from the known expansion coefficient. Taking the value for 20° C., for a change of volume of 3% or inter-atomic distance of 1%, the expected change of

frequency is 3·3% while the direct determination gives 7%. In deriving the equation on the Einstein model, the entire thermal content is ascribed to one oscillation while actually part of the energy is due to the acoustic frequencies of the crystal. The use of the experimental value of C_v therefore partly accounts for the discrepancy between observed and calculated values. But the surprisingly large change of frequency is possibly also due to the fact that the 1332 line is the lattice oscillation which causes the diamond-graphite transformation. The result is in accord with the results obtained for quartz by Nedungadi, where the particular oscillations responsible for polymorphic transition were found to show changes in frequency and breadth even at low temperatures far removed from the temperature of α–β transformation.

The diamonds used in this investigation were lent by Prof. Sir C. V. Raman from his personal collection. For this kindness and for his helpful interest in this work, the author desires to express his grateful thanks.

5. *Summary*

The frequency of the Raman line of diamond has been studied at eight different temperatures and found to vary from 1333·8 cm.$^{-1}$ at −190° C. to 1316·4 at 860° C. From the thermodynamical relation between the thermal expansion of the crystal and the variation of the characteristic frequency, it has been found that the change observed is greater than that expected. In this connection the part played by the oscillation of the lattice in the conversion of diamond to graphite at 1800° is discussed.

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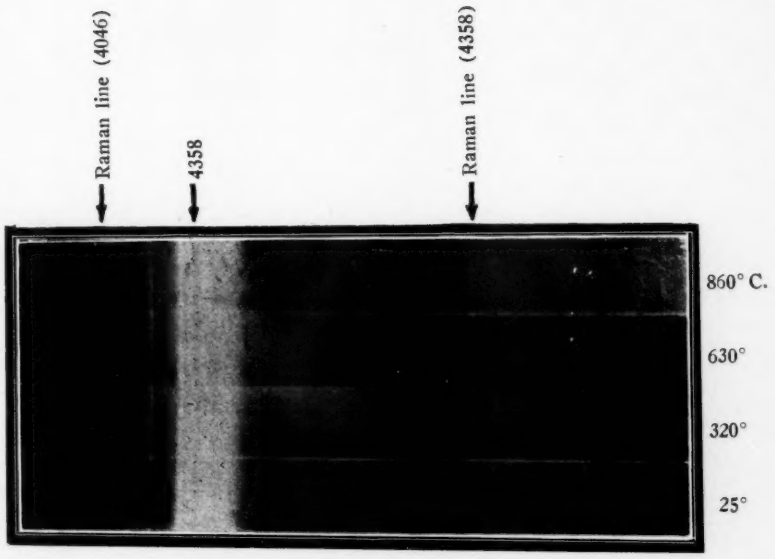

Raman Spectra of Diamond at Four Temperatures taken with a Hartmann Diaphragm

THE RAMAN SPECTRUM AND THE SPECIFIC HEAT OF CRYSTALLINE SULPHUR

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The importance of studying the Raman spectra of single crystals and the interesting facts brought to light by such a study have been stressed in several papers that have recently appeared in these *Proceedings*. A single crystal of sulphur can be easily grown to a good size, and as it scatters light strongly, is specially suitable for such work. The Raman spectrum of sulphur was first studied by Krishnamurti (1930) and later by Venkateswaran (1936), in the form of crystalline powders. Taylor and Rideal (1927), investigated the infra-red absorption of sulphur and found four absoprtion bands at $7 \cdot 76\,\mu$, $10 \cdot 73\,\mu$, $11 \cdot 9\,\mu$ and $14 \cdot 6\,\mu$; and later, Barnes (1932) measured the presence of eight other bands at $21 \cdot 5\,\mu$, $25 \cdot 0\,\mu$, $37 \cdot 5\,\mu$, $40\,\mu$ to $50\,\mu$, $67\,\mu$, $96\,\mu$, $114 \cdot 5\,\mu$ and $\lambda > 130\,\mu$. By an X-ray investigation, Mark and Wigner (1924) concluded that rhombic sulphur belongs to the space group V_h^{24} and that the unit cell contains 128 atoms grouped as 8 molecules of 16 atoms each. To explain their infra-red absorption results, Taylor and Rideal assumed the S_{16} molecule to consist of 8 (S_2) groups situated at the corners of a cube. Later, Warren and Burwell (1935) reinvestigated the structure of sulphur by the X-ray method and concluded that the unit cell contains 16 molecules of eight atoms each, the atoms being at the corners of a puckered octagon, this itself being formed of two squares set one above the other and turned through 45°. The plane of each molecule is parallel to the *c*-axis of the crystal and makes an angle of about 50° with the *a*-axis. The side of the square is 3 ·38 Å and the distance between the two squares is 1 ·15 Å, the bond angle being 105°. Assuming Warren and Burwell's model, Bhagavantam and Venkatarayudu (1938) have calculated by the group theory method, the different modes of fundamental vibrations possible in a sulphur molecule and concluded that eleven distinct modes are possible, of which, seven are Raman active and Infra-red inactive, while three are infra-red active and Raman inactive, one being inactive in both. These authors have also calculated theoretically the specific heat of sulphur. Their values, however, do not quite

agree with the experimental data, and as will be made clear later in this paper, the method of calculation is also open to objection.

The present author undertook the study of the Raman spectra of a single crystal of sulphur and of their variations with different orientations of the crystal and with the incident light in different states of polarisation. This investigation has yielded some fruitful results ; especially the observation of a new strong Raman line with a frequency shift of 50 cm.$^{-1}$, and of the behaviour of the two low frequency lines* 50 and 85, as well as the three other intense lines 216, 470 and 434 in different orientations of the crystal. Incidentally, the work has enabled a new assignment of the fundamental frequencies to be made, and a theoretical calculation of the specific heats gives values in close agreement with the experimentally determined values.

Much of the work described in this paper was completed by the summer of 1940, but remained unpublished. Meanwhile a paper by Venkateswarlu has appeared, dealing with the same subject. We shall reserve comment on his work to a later stage of the present paper.

2. *Experimental*

A clear specimen is selected from the crystals grown, and is cut and polished perpendicular to the three axial directions. Sulphur crystals being yellow, they transmit only the green and yellow radiations of the mercury arc. Ilford H.P. 2 plates were found very suitable for photographing the spectra in this region. A strong and clear spectrogram can be obtained in about eight hours with a Fuess glass spectrograph, and first the experimental results were obtained with this instrument. The investigation was later repeated with a Hilger two-prism glass spectrograph of large light-gathering power, confirming the results arrived at with the Fuess instrument. The incident light was polarised, when required, by a polaroid. The spectrograms were measured on a micrometer by comparison with an iron arc spectrum recorded on the plates.

3. *Experimental Results*

The experimental results obtained are shown in the following two tables. A few of the spectra obtained are reproduced in Plate XV. An intense line with a frequency shift of 50 cm.$^{-1}$ observed for the first time in this investigation is clearly seen in these spectra. It may be recalled that Barnes in his paper on the infra-red absorption of sulphur has mentioned the possible presence of a frequency less than 77 wave numbers. The line 114 is extremely weak. It is on account of its weak intensity that Krishnamurti in his investigation did not record this line, while Venkateswaran who observed it assigned to

* The numbers in this and subsequent pages denote the wave numbers in cm.$^{-1}$

it an intensity zero. But, Venkateswarlu states in his paper, that the line 115 is as intense as 85 and in fact assigns it an intensity of 5. In none of the several plates taken by the author for the different orientations of the crystal was this line found to appear with any appreciable intensity. Venkateswarlu also makes mention of the presence of a very faint line at 520 wave numbers which he ascribes to an internal vibration of the sulphur molecule. In the spectra obtained by the author, a faint line is observed at 17798 wave numbers which is the anti-Stokes line corresponding to frequency shift 470 excited by the first of the two strong yellow lines of the mercury arc. A stronger but diffuse band covering the region 17762 to 17732 wave numbers is also recorded. This appears to be excited by the green line 5461 Å of the mercury arc with a mean frequency shift of 556 cm.$^{-1}$ Upon this line also falls the weak anti-Stokes line corresponding to 470 cm.$^{-1}$ excited by the second of the two yellow lines of the mercury arc.

Table I gives the frequencies of the observed Raman lines with their relative intensities for an unrecorded orientation of the sulphur crystal.

TABLE I

Raman Frequencies of Sulphur Crystal

Wavelength of the observed Raman lines Å	Wave number cm.$^{-1}$	Exciting line	Raman frequencies in cm.$^{-1}$ with their relative intensities
5475·7	18257	5460·74 Å (18307·5 cm.$^{-1}$)	50 (7)
5486·2	18222	,,	85 (5)
5495·0	18193	,,	114 (½)
5506·8	18154	,,	153 (10)
5516·1	18123	,,	184 (2)
5526·0	18091	,,	216 (10)
5534·2	18064	,,	243 (2)
5593·3	17873	,,	434 (3)
5604·6	17837	,,	470 (9)
5617·0	17798	5769·60 Å (17327·4 cm.$^{-1}$)	−470 (½)
5628·4 to 5637·8	17762 to 17732	5460·74 Å	556 (1)
5637·3	17634	5790·66 Å (17264· 4 cm.$^{-1}$	−470

The effect of the orientation of the sulphur crystal upon the intensities of the Raman lines with the incident light in different states of polarisation is represented in Table II for two different orientations.

TABLE II

Effect of Orientation of the Crystal and Polarisation of the Incident Light

Incident light along *b*-axis and observation along *a*-axis; *c*-axis vertical		Incident light along *a*-axis and observation along *c*-axis; *b*-axis vertical	
Light unpolarised	Light polarised with vibration along *c*-axis	Light unpolarised	Light polarised with vibration along *b*-axis
50 (2)	50 (2)	50 (5)	50 (10)
85 (5)	85 (5)	85 (4)	85 (3)
153 (10)	153 (10)	153 (10)	153 (9)
216 (10)	216 (10)	216 (10)	216 (10)
434 (0)	434 (0)	434 (3)	434 (3)
470 (7)	470 (6)	470 (10)	470 (10)

The lines 114, 184, 243, and 556 are very weak and hence much cannot be said about them.

4. The Identification of the Fundamental Frequencies

In Table III, the observed frequencies are grouped into the different classes to which the vibration modes belong. An important point in this table is the identification of the frequency 114 as a normal frequency of the internal vibration of the molecule and not as one due to lattice vibration. The frequency at 556 cm.$^{-1}$ is attributed to the appearance in the crystalline state of a frequency which was calculated for the case of a sulphur molecule by Bhagavantam and Venkatarayudu and found to be prohibited in both the Raman effect and infra-red absorption. This appearance of a prohibited line is not surprising, as the normal modes of a group atoms forming a molecule or ion which go to build up a crystal usually undergo modifications in the way of splitting of degeneracies, multiplicity or alterations in the selection rules (Bhagavantam and Venkatarayudu, 1939). Bhagavantam and Venkatarayudu have assigned the two frequencies 470 and 216 to be the frequencies ν_1 and ν_2 due to the two symmetrical modes of vibration possible in the sulphur molecule, ν_1 being that in which the four atoms in each square move towards or away from the centre of the square

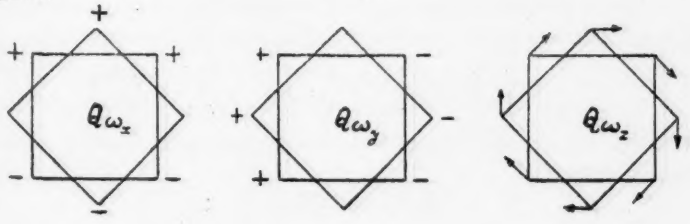
and ν_2 that in which the two squares are vibrating against each other. This view, however, is difficult to reconcile with the observation made by the author that the line 470 is weaker when the *c*-axis of the crystal is perpendicular to the plane containing the directions of incidence and observation, and stronger when it is along the direction of observation. This observation, taken together with the data for the orientation of the molecules in the crystal furnished by Warren and Burwell, indicates that 216 should be assigned to ν_1 and 470 to ν_2. This assignment is also found to be true by calculating the frequencies, by first finding the potential and kinetic energies of the molecule for these two modes and using Lagrange's equations of motion. The infra-red fundamentals are, however assigned in the following table in the same way as by Bhagavantam and Venkatarayudu with the modification introduced by Venkateswarlu.

TABLE III

Class	Observed Raman frequencies cm.$^{-1}$	Infra-red frequencies cm.$^{-1}$	Degeneracy of each frequency
A_1 ..	216, 470	*f*	(1)
B_1 ..	*f*	400 (w)	(1)
B_2 ..	(f) 556	*f*	(1)
E_1 ..	*f*	200 (st); 465 (st)	(2)
E_2 and E_3 ..	114, 153, 184, 243, 434	*f*	(2)

Of the two classes E_2 and E_3, three frequencies belong to the E_2 class and two frequencies belong to the E_3 class. In the above table *f* denotes that the particular frequency is prohibited in the case of the sulphur molecule as indicated by Bhagavantam and Venkatarayudu.

The two low frequencies 50 and 85 of the sulphur crystal are identified with the three rotational modes Q_{w_x}, Q_{w_y} and Q_{w_z} represented by the following figures.



On account of the symmetry, we have $w_x = w_y$. The sulphur molecules do not rotate freely, as they are packed together in the solid crystal. The two low frequency lines 50 and 85 may therefore be ascribed to rotational oscillations which roughly correspond to the above three modes of motion. In our directional study of the spectra of the sulphur crystal, when the incident light is polarised in a direction perpendicular to the plane of incidence and observation, we find, as will be seen clearly in Plate XV, that the line 50 is much weaker than 85 when the *c*-axis of the crystal is vertical; while, when that axis is along the direction of observation, the 50 line becomes much stronger than the 85. Assuming the orientations of the molecules in the crystal to be those indicated by Warren and Burwell, we can see immediately that this effect would arise if 50 is due to the tilting oscillation w_x and w_y and hence is also doubly degenerate, while 85 is due to the rotational oscillation w_z and single.

5. *Calculation of the Specific Heat of Sulphur*

There are two types of vibrations possible in a crystal. The first constitutes the acoustic type of elastic waves which traverse the crystal in all directions with a spectrum of frequencies ranging from 0 to an upper limit ν_m, as suggested by Debye. The second is the optical type manifesting itself as discrete frequencies in the infra-red region of the spectrum.

The sulphur molecule consists of eight atoms and hence we expect eighteen internal vibrations, some of them grouped together on account of degeneracies, and which, if not forbidden, may be observed in the infra-red absorption or Raman scattering. For the calculation of the molecular specific heat of sulphur, we take the Einstein functions of these eighteen discrete frequencies, taking into account the degeneracies indicated by theory. We also consider the contribution towards the specific heat due to the three rotational oscillations whose frequencies are indicated by the low frequency shifts ; and as these low frequencies appear as discrete lines, we take their Einstein functions. The remaining three degrees of freedom correspond to the linear translations of the molecules which give rise to the acousitc waves of the Debye theory. Hence their contribution towards the specific heat is taken as a Debye function corresponding to three degrees of freedom. Hence the gramme-molecular heat of solid sulphur may be represented as

$$C_v = D\left(\frac{\theta}{T}\right) + \frac{1}{3}\sum_{r=1}^{r=3} E\left(\frac{\theta_r}{T}\right) + \frac{1}{3}\sum_{l=1}^{l=18} E\left(\frac{\theta_l}{T}\right)$$

As mentioned before, the frequencies that go under the second term in the above equation are:

50 (2) and 85 (1) ;

while those that go within the third term are :

114 (2); 153 (2); 184 (2); 200 (2); 216 (1); 243 (2); 400 (1); 434 (2); 465 (2); 470 (1); 556 (1).

The numbers within brackets represent the degeneracies in each case.

As the elasticity data of sulphur are not available for calculating the mean effective characteristic temperature θ of the Debye function, this is found once for all by considering the experimentally observed value of the specific heat at any sufficiently low temperature and subtracting from it the sum of the contributions due to the second and third terms in the above equation. For instance, the value of C_p observed at $T = 10°$ K which $= 2 \cdot 48$ is made use of here. Since the C_v due to Einstein terms itself amounts to $0 \cdot 16$, C_v due to the Debye term $= 2 \cdot 32$ from which we get $\theta = 47° \cdot 7$ which corresponds to $\nu_m = 33$ cm.$^{-1}$. This fixed value of θ in the Debye term is made use of for all the other temperatures.

For the calculation of the value of $(C_p - C_v)$ at the different temperatures, use is made first of the well-known thermodynamic relation,

$$C_p - C_v = \frac{\alpha^2 VT}{\beta},$$

α being the coefficient of thermal expansion, and β being the coefficient of compressibility.

For sulphur, we have at room temperature, for $T = 300°$K, $\alpha = 3 \times 0 \cdot 64 \times 10^{-4}$ per degree and $\beta = 12 \cdot 5 \times 10^{-12}$ sq. cm. per dyne. Thus, $(C_p - C_v) = 2 \cdot 6$ calories per gramme molecule at $T = 300°$K. As the values of α and β at different temperatures are not known for sulphur, $(C_p - C_v)$ for the various different temperatures, cannot be calculated directly from the above formula. However, use is made of the result established experimentally and theoretically by Grüneisen that the coefficient of expansion is proportional to the specific heat at constant volume, and of the fact that the specific volume and the compressibility vary little with temperature. The above formula then becomes

$$C_p - C_v = A\, C_v^2\, T.$$

Making use of this formula and the known values of $(C_p - C_v)$ and C_v at $T = 300°$K, the constant A can be calculated, knowing which the $(C_p - C_v)$ values are calculated for the other temperatures. The values thus calculated are shown in Table IV.

TABLE IV

Specific Heat of Sulphur

Temperature K	D $\left(\frac{47\cdot7}{T}\right)$	C_v rotational	C_v internal vibrations	$(C_p - C_v)$	Total Specific Heat calculated	Total Specific Heat observed*
10	2·32	0·16	0		2·48	2·48
20	4·54	1·66	0·09		6·29	5·76
30	5·28	3·11	0·79	0·01	9·19	9·20
40	5·56	4·04	2·22	0·02	11·84	11·26
50	5·70	4·59	4·14	0·05	14·48	14·16
60	5·78	4·96	6·23	0·08	17·05	16·64
70	5·82	5·21	8·25	0·12	19·40	19·04
80	5·85	5·36	10·24	0·17	21·62	21·44
90	5·87	5·49	12·01	0·24	23·61	23·52
100	5·88	5·56	13·73	0·31	25·48	25·60
150	5·93	5·78	20·59	0·75	33·05	32·80
200	5·93	5·86	24·98	1·27	38·04	37·52
250	5·94	5·88	27·99	1·97	41·78	41·04
300	5·95	5·91	29·91	2·60	44·37	44·56

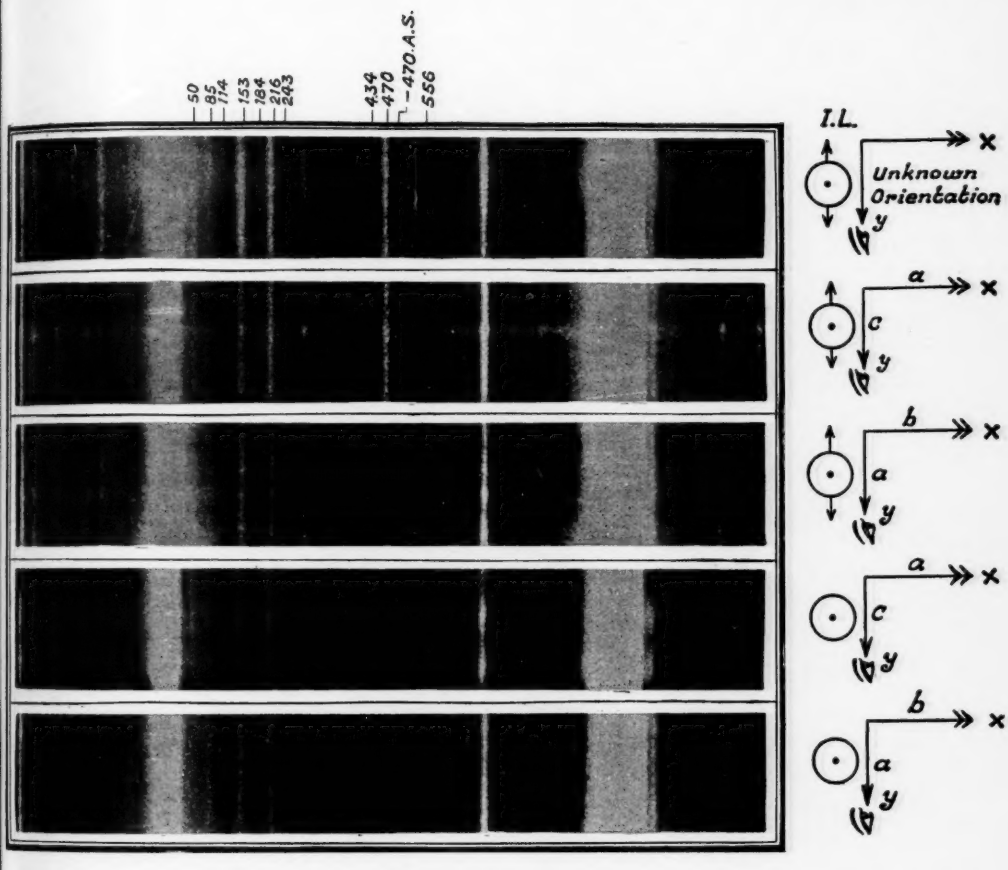
* From I.C.T., 5, *Nernst, Ann. d. Phys.*, 1911, 36, 395.

It is seen that the calculated values agree well with the observed values.

In conclusion, the author desires to thank Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his keen interest in this work. He also wishes to thank Mr. T. M. K. Nedungadi for his kind advice and assistance.

Summary

The Raman spectra of a single crystal of sulphur, are studied with special reference to their behaviour in different orientations of the crystal and with the incident light in different states of polarisation. The presence of an intense low frequency line with a frequency shift of 50 wave numbers is reported here for the first time. As indicated by the behaviour of the low frequency lines 50 and 85 in different orientations of the crystal, and with the incident light in different states of polarisation, they are assigned respectively



Raman Spectra of Sulphur Crystal

to the tilting and rotational oscillations of the sulphur molecule. The modes of symmetric vibration of the S_8 molecule corresponding to the lines 216 and 470 are also thus determined. The specific heat of sulphur is represented as the sum of three expressions. The first is a Debye function for the continuous acoustic waves, the second represents the sum of Einstein functions for the rotational oscillations of the S_8 molecule, and the third represents the sum of the Einstein functions for its internal vibrations. The values thus calculated are found to agree well with the observed values of the specific heat of sulphur.

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THE THERMAL CONDUCTIVITY OF INDIAN TIMBERS

Part I. Variation of Conductivity with Density in the Air-Dry Condition at Ordinary Temperature

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Received February 4, 1941

Introduction

The thermal conductivity of wood is an important property. As remarked by Cammerer (1938) while for good thermal insulating properties a substance should be porous, good strength properties on the other hand demand a compact structure. Structural and insulating materials should therefore satisfy both the requirements. Wood in this respect is in a specially advantageous position, for, in its case, the relation between thermal insulation and strength is extraordinarily favourable. Its low thermal conductivity makes it an ideal material for house construction, water pipes, tanks, casings, railway and other carriages, drying chambers, cold rooms, etc. Further, thermal conductivity in conjunction with volumetric specific heat determines the rate of temperature change in wood when it is heated or cooled. A knowledge of this is of interest and importance for studies in preservation, sterilisation, fire resistance, the drying of wood and in the making of plywood. Despite the importance of the thermal properties of wood accurate data on these properties are lacking to a large extent. Such few reliable data as may be available refer to European or American timbers. Apart from a small number of measurements carried out by Narayanamurti (1935) no data at all is available with regard to Indian timbers. The data published by Rowley (1933) for American woods deal with a density range of 409 Kg./m.^{3} to 745 Kg./m.^{3} Other data with regard to non-Indian timbers reported in the literature are not complete, in that the moisture content, temperature, density, etc., are not always given (*cf. The International Critical Tables*, Vol. II). Moreover, often the work has been carried out without taking all the necessary precautions one has to observe when dealing with timber.

In view of the above, it is the intention to investigate the thermal properties of Indian timbers in detail, and the present paper deals with the

thermal conductivity of 56 timbers in the air-dry condition, varying in density from 265 Kg./m.^{3} to 1310 Kg./m.^{3} Future communications will deal with the effect of moisture content, temperature, etc.

The Apparatus.—The apparatus used in the investigation is schematically shown in Fig. 1. It is a guard-ring apparatus and is suitable for the measurement of the thermal conductivity of not only wood and similar materials but

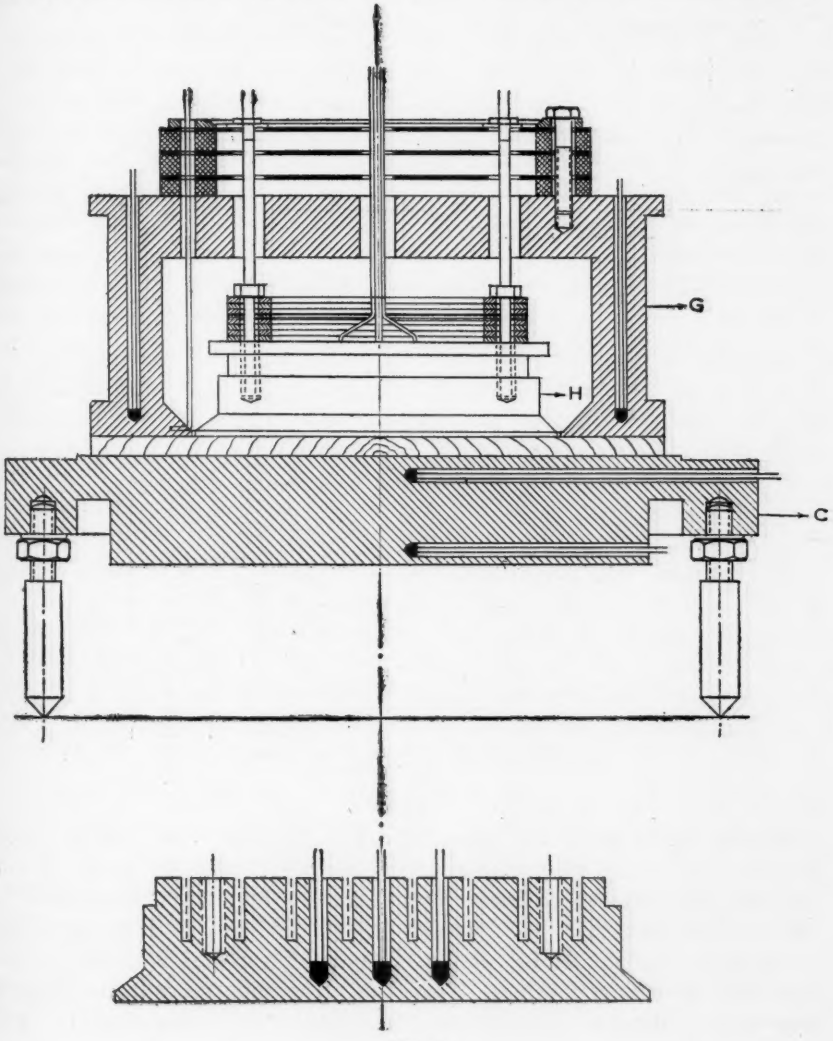


FIG. 1

also liquids. It differs from the usual guard-ring apparatus used in such studies in that it is a single plate apparatus. It is made of copper and consists of a cold-plate C on which the specimen to be tested is placed, and a hot-plate H of about 10 cm. diameter. The guard-ring G is shaped like a dome and is maintained at the same temperature as the hot-plate, the space between the upper surface of the hot-plate (which is also insulated) and the inner surface of the top of the guard dome being filled with air.

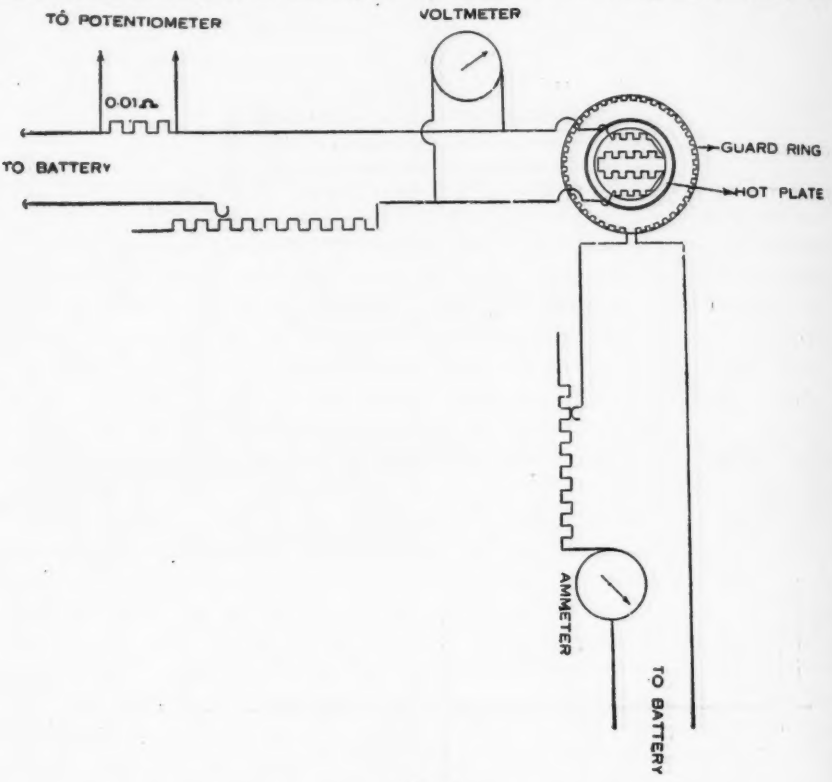


FIG. 2

Hot-plate, guard dome and specimen can be brought when required under a bell jar which sits on the outer rim of the cold-plate. By means of suitable salt solutions placed inside the bell jar any humidity corresponding to the moisture content of the specimen being tested can be maintained, thus avoiding any danger of the drying of the specimen during the test, which will result in incorrect values. This is of great importance in the study of hygroscopic materials and has been neglected by previous workers which

sometimes led to erroneous results (especially at high moisture contents). Despite the fact that the apparatus is made of copper every care was taken in the design of the heating coil for the hot-plate so that the heating will be uniform throughout the plate. By the circulation of water of constant temperature the cold-plate was maintained at any desired temperature. A battery of accumulator cells of sufficient capacity was used, as the source of energy.

Material Used and the Preparation of the Test Specimens.—Fifty-six species of air-seasoned timbers that were available at the Forest Research Institute were included in this study. It is proposed to investigate other important timbers, as also the influence of the locality of origin, in the near future. The specimens were made from the heart-wood of the various species by the Wood Working Section and were kindly identified by the Wood Technologist of this Institute. The surfaces were made as smooth as possible. In order to avoid any error that might be caused by any slight irregularity that was still present the method of mounting the specimen devised by Narayanamurti (1936) was adopted.

Measurement of Temperature.—For the measurement of temperature, calibrated soft soldered manganin-constantan thermocouples (0·3 mm. diameter) were employed. The hot-plate was provided with three thermocouples, one embedded in the centre of the plate and the other two at points on either side of the centre on a diameter. In the case of the guard dome temperatures were measured at three points (being the apices of an equilateral triangle), at two points by means of thermocouples and at the third place by means of a standard mercury thermometer, thus ensuring a check on the calibration during any experiment. In the case of the cold-plate the temperature was likewise measured at three points by means of suitably located thermocouples. For the measurement of the thermal e.m.f.s a Tinsley Diesselhorst thermo-electric potentiometer with a Tinsley galvanometer of about 10 ohms coil resistance and a deflection of 130 millimetres at 1 metre per micro-ampere as null instrument was used.

Measurement of Energy.—The electrical energy supplied for the production of heat was measured in two ways: In some experiments the current in the hot-plate coil and the potential difference across its terminals were measured with the help of a Siemens precision volt- and ammeter with the necessary shunts and series resistances. In the second method the current was measured by determining the potential difference across a 0·01 ohm standard resistance connected in series with the hot-plate coil. This potential difference was measured by means of the Diesselhorst potentiometer. The

potential difference across the heating coil was measured in this case also with the help of the precision voltmeter.

Measurement of Thickness, etc.—The thickness of the specimens was measured at a number of places by means of vernier callipers or micrometer screw gauge and the average taken. In addition, by measuring the area of the specimen and weighing it, its volume and density were calculated. For the determination of the moisture content the oven drying method was adopted.

Accuracy of the Measurements.—Temperature measurements could be read to an accuracy of 0·01° C. with ease. The measurement of the heat input was accurate to 0·2%, as a calibrated precision instrument was used and 0·1 division of a division in a range of 150 scale divisions could be read. While individual measurements of the thickness were accurate to 0·1%, the variation between the mean and the individuals was higher. On the whole it is estimated that the conductivity values are accurate to 1% in most cases and 2% in the unfavourable cases.

Experimental Procedure.—The general procedure of carrying out a test was to put the specimen in the apparatus, when the heat supply was switched on and adjusted from time to time till the desired temperature was attained for the hot-plate. Care should be taken not to heat the plate above the desired temperature. It was therefore brought up to that temperature slowly. With moist materials there is a movement of moisture whenever a temperature gradient exists and if the temperature of the hot-plate is above the desired experimental temperature, errors may be caused due to this moisture movement. To cut down this movement of moisture to a minimum, a temperature difference of about 6° C. on an average was used. Theoretical calculations of Krischer (1934) show that as long as the ratio of the thermal conductivities of the extreme boundary layers of the material does not exceed 2, the value obtained does not deviate from the true value significantly. When the ratio is 2, the deviation from the correct value is 3·5%, it being considerable when the ratio exceeds 2. The temperature of the guard dome was also brought to the same temperature as that of the hot-plate by careful adjustment of the current in its heating coils. The apparatus was then left undisturbed with a constant energy input from the battery. Readings of temperature, current and voltage were taken once every fifteen minutes or half an hour and after the steady state was reached observations were continued for a further period of at least about two hours.

Evaluation of the Experimental Data.—For the calculation of the thermal conductivity the following equation was used:

$$k = \frac{d \cdot Q}{A\,(t_1 - t_2)},$$

where k is the thermal conductivity in K.cal./m. h. °C.,

d is the thickness of the specimen in m,

A is the effective area of the specimen in m^2,

Q is the heat energy produced in the hot-plate in K.cal./h.,

t_1 is the mean temperature of the hot-plate in °C., and

t_2 is the mean temperature of the cold-plate in °C.

The method of evaluation of the experimental data can best be illustrated by means of a typical example.

Example of the evaluation of the experimental data for Michelia *Sp.*: *Experiment carried out on* 24–2–1940. *Direction of heat flow*: Radial.

Heating current	Mean value of the e.m.f. of the thermocouples	
0·140 amp., 4·83 volt.	Hot-plate 0·987 mv.	Cold-plate 0·713 mv.
Mean temperatures	0·987 mv.= 23·30° C.	0·713 mv.= 17·15° C.

Thickness of the specimen	d= 0·01009 m.
Effective area of the specimen	A= 0·008079 $m.^2$
Mean temperature of the hot-plate	t_1= 23·30° C.
Mean temperature of the cold-plate	t_2= 17·15° C.
Temperature difference between the hot-plate and the cold-plate ..	$t_1 - t_2$= 6·15° C.
Watts dissipated	E.I.= 4·83× 0·14 watt = 0·6762 watt
Voltmeter correction	$\frac{(4\cdot83)^2}{5000}$= 0·00467 watt
Corrected heat input	= 0·6715 watt

Thermal conductivity according to equation

$$(1)\ k = \frac{d.\ Q}{A\,(t_1 - t_2)} = \frac{0\cdot01009}{0\cdot008079} \cdot \frac{0\cdot6715 \times 0\cdot86}{6\cdot15} = 0\cdot1172 \frac{\text{K.cal.}}{\text{mh °C.}}$$

Results and Discussions

The results of all measurements are given in Table I. The conductivity is represented as a function of the density in Fig. 3, and as a function of

TABLE I

No.	Species of timber	Direction of heat flow	Moisture content %	Mean temperature °C.	Density* Kg/m.³	Percentage air space	Thermal conductivity K cal/mh °C.
1	*Bombax* sp.	Radial	12·2	20·78	265·0	81·4	0·07342
2	*Cryptomeria japonica* ..	do.	9·7	20·47	287·0	79·97	0·07513
3	do. ..	do.	..	20·39	304·0	..	0·08012
4	*Bombax* sp.	do.	..	31·0	400·0	..	0·08751
5	*Erythrina* sp.	do.	11·7	20·52	427·0	70·05	0·0871
6	*Gmelina arborea*	do.	8·8	20·53	431·0	69·99	0·1014
7	*Anthocephalus cadamba* ..	Radial-Tangential	9·8	20·72	439·0	69·36	0·1043
8	*Abies pindrow*	do.	13·0	20·66	442·8	68·85	0·0959
9	*Pinus longifolia*	do.	12·9	20·21	444·0	68·77	0·0959
10	*Machilus* sp.	do.	11·0	20·11	459·0	67·87	0·1012
11	*Pinus excelsa*	do.	..	20·40	480·0	..	0·0933
12	*Terminalia* sp.	do.	8·0	20·57	522·0	63·72	0·0988
13	*Cedrus deodara*	do.	7·0	21·00	542·0	62·42	0·1124
14.	*Swintonia* sp.	do.	10·0	20·49	559·0	60·96	0·1190
15	*Michelia* sp.	Radial	12·1	20·23	564·0	60·40	0·1172
16	*Cupressus torulosa*	do.	13·2	20·50	570·0	59·86	0·1143
17	*Picea morinda*	Tangential	14·0	20·94	571·0	59·68	0·1034
18	*Terminalia* sp.	Radial-Tangential	10·4	20·35	586·0	59·05	0·1063

19	*Adina cordifolia*	Tangential	9·6	20·17	593·0	..	0·1281
20	*Morus* sp.	Radial-Tangential	11·1	20·80	625·0	56·24	0·1434
21	*Artocarpus* sp.	Tangential	11·7	20·45	643·0	54·92	0·1395
22	*Holoptelea integrifolia* ..	Radial	7·7	30·04	651·9	54·72	0·1448
23	*Cedrela toona*	Tangential	10·5	20·22	672·0	53·02	0·1474
24	*Tectona grandis*	do.	10·8	20·22	672·0	52·98	0·1222
25	*Pentace* sp.	Radial	10·3	20·95	675·0	52·83	0·1360
26	*Parashorea stellata* ..	Radial-Tangential	11·7	20·56	679·0	52·39	0·1284
27	*Calophyllum* sp.	do.	13·9	20·74	684·0	51·75	0·1370
28	*Albizzia* sp.	do.	12·0	20·23	685·0	51·93	0·1264
29	*Schima wallichii*	do.	13·1	20·35	737·0	48·13	0·1308
30	*Albizzia* sp.	do.	11·6	20·09	754·0	47·14	0·1458
31	*Amoora* sp.	Radial	10·9	27·95	755·0	47·17	0·1485
32	*Pterocarpus marsupium* ..	do.	..	20·31	755·0	..	0·1722
33	*Lagerstroemia* sp.	Tangential	13·2	20·81	767·0	46·00	0·1400
34	*Dalbergia latifolia*	Radial	10·6	20·50	779·0	45·52	0·1828
35	*Albizzia* sp.	Tangential	12·5	23·70	798·0	43·93	0·1641
36	*Palaquium* sp.	Radial-Tangential	13·1	20·18	806·0	43·28	0·1514
37	*Stereospermum* sp.	Radial	11·8	20·15	808·0	43·32	0·1473
38	*Bischofia javanica*	Tangential	14·2	20·22	808·0	42·97	0·1472
39	*Carallia lucida*	Radial	9·0	20·55	809·0	43·65	0·1484
40	*Pentace* sp.	do.	10·6	20·48	816·4	42·89	0·1390

* The density values relate to whole specimens and are accurate to 2 to 3%.

TABLE I (*Contd.*)

No.	Species of timber	Direction of heat flow	Moisture content %	Mean temperature °C.	Density Kg/m.^{3}	Percentage air space	Thermal conductivity K cal/mh °C.
41	*Terminalia* sp.	Radial	12·8	20·44	865·0	39·17	0·1523
42	*Homalium* sp.	Radial-Tangential	12·8	22·54	867·0	39·03	0·1884
43	*Pterocarpus macrocarpus* ..	Radial	9·2	20·70	894·0	37·70	0·1813
44	*Quercus* sp.	Tangential	12·4	19·66	897·0	36·99	0·1631
45	*Terminalia* sp.	Radial	10·9	19·92	898·0	37·15	0·1618
46	*Dalbergia sissoo*	Tangential	10·2	20·01	916·0	36·01	0·1901
47	*Anogeissus* sp.	Radial-Tangential	11·5	22·73	953·0	33·21	0·2029
48	*Terminalia tomentosa* ..	Radial	12·0	20·45	972·0	31·78	0·1987
49	*Carapa* sp.	do.	11·0	20·58	975·0	31·75	0·1969
50	*Dipterocarpus* sp.	Radial-Tangential	13·1	20·04	1014·0	28·65	0·1846
51	*Dalbergia* sp.	Radial	9·4	20·35	1027·0	28·39	0·2026
52	*Todallia bilocularis* ..	do.	12·1	23·91	1038·0	27·12	0·2132
53	*Hopea* sp.	Tangential	13·0	20·53	1064·0	25·13	0·2014
54	*Dalbergia* sp.	Radial	8·5	25·55	1070·0	25·54	0·2100
55	*Millettia* sp.	do.	8·9	19·87	1080·0	24·79	0·2119
56	*Xylia* sp.	do.	11·6	20·24	1112·0	22·05	0·2139
57	*Hardwickia binata*	Radial-Tangential	12·9	20·42	1156·0	18·45	0·2271
58	*Diospyros ebenum*	Radial	12·9	20·35	1310·0	7·89	0·2286

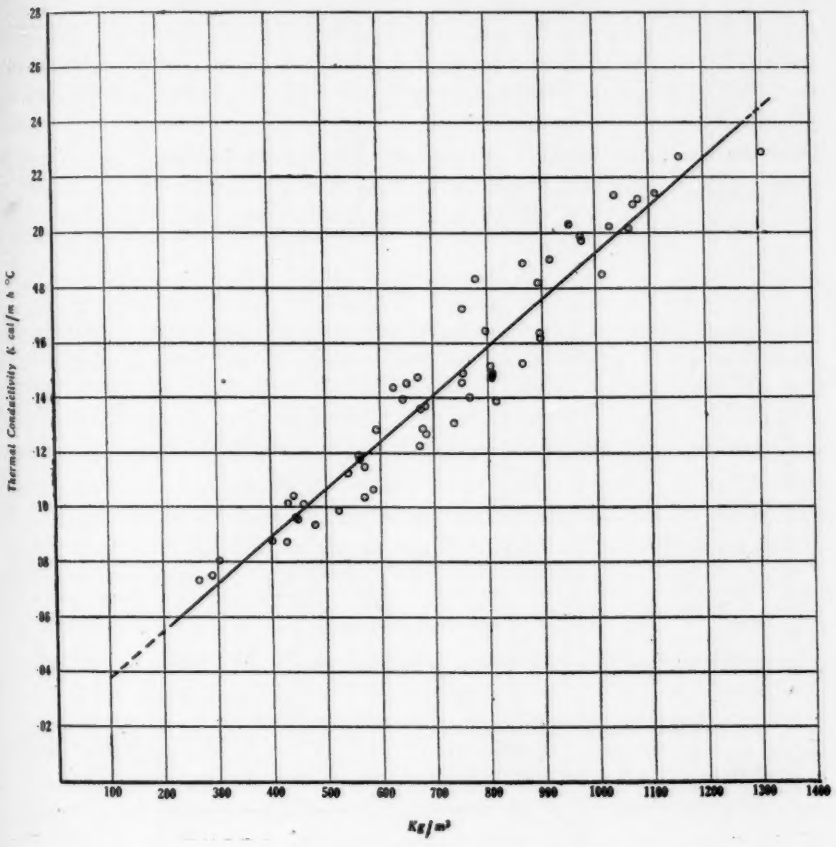
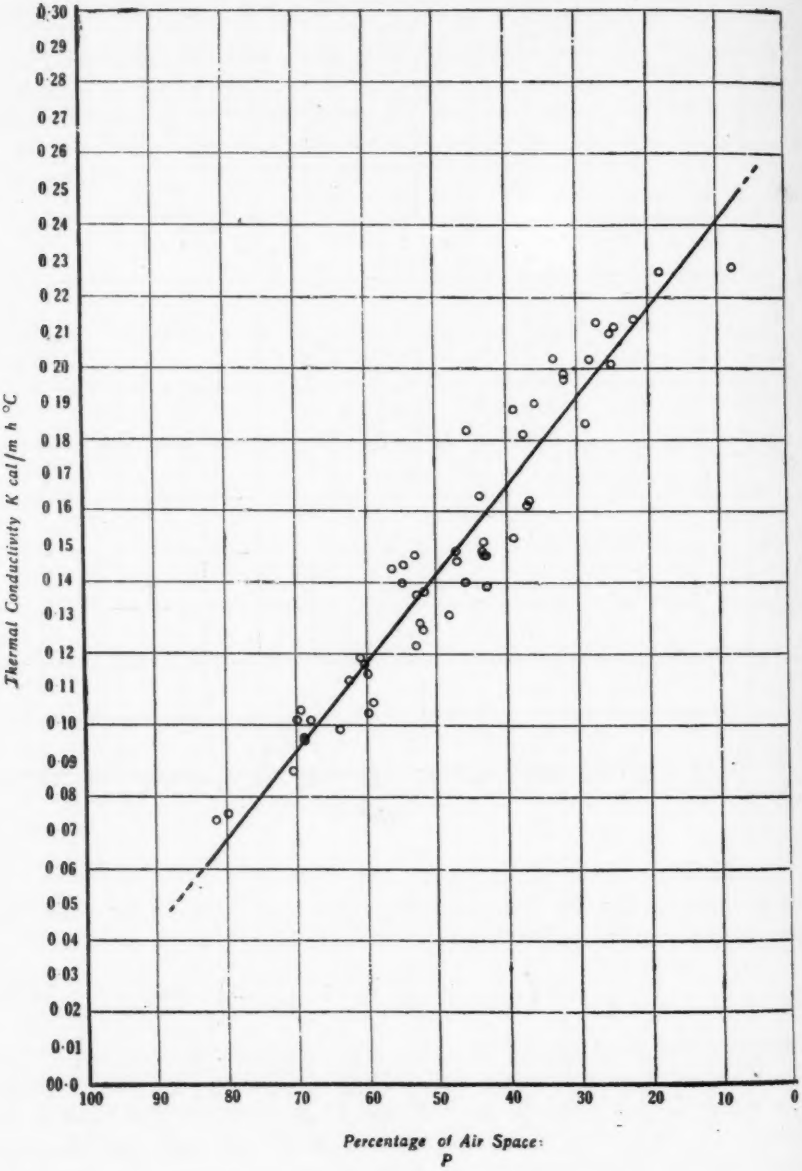


FIG. 3

the porosity in Fig. 4. The percentage of the air space in the wood was calculated according to MacLean's (1938) formula:

$$P = \left[1 - S\left(\frac{1}{1{\cdot}46} + \frac{M_f}{(100)\ d_f} + \frac{M_a}{(100)\ d}\right)\right] 100, \qquad (2)$$

where P is the percentage of air space, S is the specific gravity of the wood based on the oven-dry weight and volume at current moisture content, d_f is the density of water in the cell walls, d the density of the water in the cell cavities, M_f the percentage of moisture in the cell walls and M_a is the percentage of moisture above the fibre saturation point. The density of wood substance is taken as 1·46 g./cm.^{3}


0·30
0 29
0·28
0 27
0 26
0 25
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0 17
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0 13
0 12
0 11
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0 08
0 07
0 06
0 05
0 04
0 03
0 02
0·01
00·0
Thermal Conductivity K cal/m h °C
100
90
80
70
60
50
40
30
20
10
0
Percentage of Air Space
P

FIG. 4

The measurements reported cover a density range of 265 Kg./m.^{3} to 1310 Kg./m.^{3}, and perhaps represents the first set of values covering this entire range from a single laboratory. The percentage air space in the timbers studied varied from 7·89 to 81·4. The conductivity appears to be a linear function of the density. The graph is similar to those of Cammerer (1938), Rowley (1933) and Metz (1936). Kollmann (1934) on the other hand believes that the ralationship between thermal conductivity and density is best represented by the following empirical relationship:

$$k = 0{\cdot}15\left(\frac{R}{1000}\right) 1{\cdot}5 + 0{\cdot}04. \qquad (3)$$

According to Kollmann, the constant factor 0·4 is the value for the limiting case of zero density, *i.e.*, when the pore volume is 100%. This he believes to be the value for air under the conditions of convection and radiation that can be expected for wood pores. If the curve in Fig. 3 is extrapolated it cuts the conductivity axis at about 0·2 which is considerably less than the value given by Kollmann but rather close to the conductivity of still air. Following Schmidt (1927) the apparent conductivity k_w may be considered to be the sum of the conductivity of the substance k, the conductivity due to convection k_k and the conductivity due to radiation k_s. Thus

$$k_w = k + k_k + k_s. \qquad (4)$$

According to Kraussold (1934) the ratio of the heat transmitted by convection to that transmitted by pure conduction k_k/k for plane and cylindrical air layers can be represented as a function of the product of the Grashof and Prandtl numbers (Gr. Pr.). It can be shown (*cf.* Schmidt, 1936) that for an air layer of 1 cm. in thickness the increase in conductivity due to convection is only about 10%, and for an air layer of 1 mm. thickness it is practically zero. Schmidt (1927) expresses the conduction due to radiation by

$$k_s = \frac{d\,C_s}{1/E_1 + 1/E_2 - 1} \quad \frac{\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4}{T_1 - T_2}, \qquad (5)$$

where $C_s = 4{\cdot}96$ K.cal./m.^{2}h. degree^4 is the black body radiation constant, T_1 and T_2 the absolute temperatures and E_1 and E_2 the emissivities of the surfaces which are in radiative exchange. With $E = 0{\cdot}9$ for wood it is seen that for air layers 0·5 mm. in thickness k_s is 0·00205 K.cal./m.h. °C. and k_k is zero. Under these conditions k_w will be

$$k_w = k + k_k + k_s = 0{\cdot}0215 + 0{\cdot}0 + 0{\cdot}00205 \text{ K.cal./m.h. °C.}$$
$$= 0{\cdot}02355 \text{ K.cal./m.h. °C. at 20 °C.}$$

It must be pointed out, however, that the problem has here been simplified by assuming the pores to be bounded by parallel surfaces perpendicular to the direction of heat flow. It is proposed to go into the subject in detail when more data have been accumulated. The diameters of wood cells are on the average less than 0·5 mm. The limiting value of 0·04 given by Kollmann appears to be improbable and the figure obtained in the present investigation appears to be nearer the theoretical value to be expected. In addition, a great majority of the experimental points lie above Kollmann's curve indicating that the relationship proposed by him does not correctly represent the experimental data.

Coming to the results of the present experiments it is interesting to note that the values for *Abies pindrow* and *Pinus longifolia*, *Albizzia* sp. (No. 30) and *Amoora* sp. (No. 31), *Stereospermum* sp., *Bischofia javanica* and *Carallia lucida*, *Quercus* sp. and *Terminalia* sp. (No. 45), *Terminalia tomentosa* and *Carapa* sp. show good agreement even though the tests were carried out on different days. On the other hand, differences in the values for timbers of the same density are noticeable, *e.g.*, *Cupressus torulosa* and *Picea morinda*, *Cedrela toona* and *Tectona grandis*, *Calophyllum* sp. and *Albizzia* sp. (No. 28), *Albizzia* sp. (No. 30) and *Pterocarpus marsupium*, and *Terminalia* sp. and *Homalium* sp. Among the specimens tested the *Terminalias*, *Tectona grandis*, *Schima wallichii*, *Carallia lucida* and *Pentace* sp. (No. 40) had a comparatively low value, while *Dalbergia latifolia* and *Pterocarpus marsupium* showed a high value, thus indicating that while a general density-conductivity relationship exists some species and specimens may show a fairly wide variation from the values demanded by this relationship. It is possible that various species can be divided into groups where the variation of conductivity with density, etc., will follow the same relationship. But a large volume of data will have to be accumulated before attempting any such analysis.

Comparison with the Results of Other Investigators.—Values for European and American timbers reported by Griffiths and Kaye (1924) and Rowley (1933) are given for comparison in Table II. The agreement with the results of the present investigation in general may be considered to be good, Rowley's values being in closer agreement than the results of Griffiths and Kaye. For the densities of timbers studied by Rowley the conductivity values read from the curve, Fig. 3, give values in satisfactory agreement with the experimentally determined values and the latter values are more or less evenly distributed on both sides of the curve. On the other hand, the values derived from Kollmann's curve are all lower than the experimentally determined values. As mentioned while discussing the results, sometimes for

TABLE II

Thermal Conductivity across the Grain of Different European and American Woods

Authority: 1–19, Griffiths and Kaye; 20–41, Rowley

No.	Species of timber	Direction of heat flow	Moisture content %	Mean temperature °C.	Density Kg. m.^{3}	Thermal conductivity Kcal/m.h.°C
1	Balsa	Tangential	13·0	20	100·0	·0396
2	Spruce	Radial	16·0	„	410·0	·1045
3	do.	Tangential	16·0	„	410·0	·0900
4	do.	Radial	16·2	„	410·0	·0871
5	do.	Tangential	16·2	„	410·0	·0853
6	Cedar	do.	13·0	„	480·0	·0972
7	Fir	Radial & Tangential	15·0	„	600·0	·1008
8	Oak	Tangential	14·0	„	600·0	·1008
9	Walnut	Radial	12·0	„	650·0	·1260
10	do.	Tangential	12·0	„	650·0	·1188
11	Mahogany	Radial	15·0	„	700·0	·1440
12	do.	Tangential	15·0	„	700·0	·1332
13	do.	Radial	14·9	„	700·0	·1498
14	do.	Tangential	12·7	„	700·0	·1393
15	Teak	do.	10·0	„	720·0	·1188
16	Ash	Radial	16·0	„	740·0	·1670
17	do.	Tangential	16·6	„	740·0	·1498
18	do.	Radial	15·0	„	740·0	·1512
19	do.	Tangential	15·0	„	740·0	·1404
20	Cedar, western ..	Across the grain	12·0	24	410·5	·0893
21	Fir, white	do.	„	„	400·5	·0806
22	Pine, sugar	do.	„	„	408·5	·0856
23	Redwood	do.	„	„	416·5	·0942
24	Spruce, sitka ..	do.	„	„	425·5	·0843
25	Pine, northern white ..	do.	„	„	440·6	·1029

TABLE II (*Contd.*)

No.	Species of timber	Direction of heat flow	Moisture content %	Mean temperature °C.	Density Kg. m.^{3}	Thermal conductivity Kcal/m.h.°C
26	Hemlock, eastern ..	Across the grain	12·0	24	456·5	·0992
27	do. western ..	do.	,,	,,	456·5	·0942
28	Cypress, southern ..	do.	,,	,,	464·6	·1029
29	Pine, Norway ..	do.	,,	,,	480·6	·1042
30	do. ponderosa ..	do.	,,	,,	488·6	·1054
31	Elm (soft)	do.	,,	,,	520·6	·1128
32	Douglas fir	do.	,,	,,	528·6	·0955
33	Pine, short-leaf ..	do.	,,	,,	544·7	·1215
34	do. long-leaf ..	do.	,,	,,	608·7	·1191
35	Larch, western ..	do.	,,	,,	624·7	·1227
36	Maple (soft) ..	do.	,,	,,	624·7	·1300
37	Ash, white	do.	,,	,,	640·8	·1302
38	Birch, yellow ..	do.	,,	,,	688·8	·1240
39	Maple (hard) ..	do.	,,	,,	712·9	·1438
40	Oak, red	do.	,,	,,	720·9	·1488
41	do. white	do.	,,	,,	744·9	·1513

Rowley's values taken from the *Wood Hand-book*, U.S. Dept. of Agriculture, September 1935, p. 44.

the same density appreciable differences in the conductivity values are also noticeable in the results of Rowley as well as of Griffiths and Kaye.

Summary

Accurate data on the thermal conductivity of 56 species of Indian timbers, varying in density from 265 Kg./m.^{3} to 1310 Kg./m.^{3} in the air-dry condition at about 20° C., are reported.

The data represent the first set of results covering this entire range of density reported from a single laboratory.

The influence of convection and radiation on the conductivity of wood is discussed and the results compared with those of other investigators.

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THE REMARKABLE FLUORESCENCE OF CERTAIN COUMARIN DERIVATIVES

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In a previous paper[1] the important structural features that affect the fluorescence of hydroxycoumarins and chromones were discussed. Amongst coumarin derivatives certain 3-carbethoxy and 3-carboxyumbelliferones exhibited remarkable fluorescence; besides the intensity being great the fluorescence was very prominent and bright even in neutral alcoholic solutions. Hence it became a matter of interest to test if besides the above two groups others containing a carbonyl would give rise to the same effect and further if the remarkable capacity of these 3-substituted compounds to fluoresce in neutral solution would persist even after the 7-hydroxy group is modified by etherification. The present paper records the synthesis of a number of derivatives of 7-hydroxycoumarin not prepared till now. They are prepared from β-resorcylic aldehyde, orcylic aldehyde and 4-O-methylresorcylic aldehyde the last of which occurs in several plant materials by condensation with ethyl acetoacetate, ethyl benzoylacetate and diethyl malonate using piperidine as the condensing agent. The preparation and properties are briefly embodied in Table I. A detailed study of their properties has been made with particular reference to the fluorescence exhibited by them in neutral, alkaline and acid solutions. Also for purposes of comparison a number of previously known compounds have been re-examined for their fluorescence under the same conditions as adopted for the new compounds. The results are discussed towards the end of this paper.

Experimental

The condensations of the hydroxy-aldehydes with the esters were effected in the presence of piperidine. The practical details were nearly the same in all the cases but for some slight modifications in the method of purification. The following is a typical experiment:—

A solution of orcylic aldehyde (0·1 g.) and ethyl acetoacetate (5 drops) in alcohol (1 c.c.) was treated with piperidine (3 drops) and the resulting solution left overnight in a stoppered test-tube. It was then rendered acid

with dilute hydrochloric acid when a solid separated out contaminated with some oily matter. After pouring out the aqueous solution the mixture was stirred with ether (10 c.c.) when the oily impurity alone dissolved leaving behind a better-looking solid. The clear supernatant liquid was decanted off and the residual solid washed again with ether (10 c.c.) by decantation. Two crystallisations from hot alcohol gave 3-acetyl-5-methyl-7-hydroxy-coumarin in the form of rhombic and rectangular plates melting at 224–25°.

The reactants for the preparation of the other coumarin derivatives, their physical properties and chemical composition are summarised in Table I. The sample of 4-O-methyl-resorcylic aldehyde used in the preparation of the 7-methoxy-coumarins was obtained from the root of *Decalepis Hamiltonii*[2]. 3-Carboxy-7-methoxy-coumarin was obtained from the 3-carbethoxy compound by treatment with cold 10% alcoholic potash during 24 hours. In all cases alcohol was used as the solvent for the crystallisations.

The visible fluorescence of the compounds was studied in very dilute solutions under illumination by daylight. First the colours in concentrated sulphuric acid and in alcoholic solutions were observed; subsequently part of the alcoholic solution was rendered faintly acid with one drop of dilute sulphuric acid and another part alkaline with one drop of dilute sodium hydroxide. It was noticed in all cases that dilution of the alcoholic solution with tap water (pH 7·2) produced an effect which was comparable to that of the addition of alkali; this effect was not observed when distilled water was the diluent.

To test if the organic solvent employed had any marked influence on the fluorescence exhibited by these 3-substituted coumarins the behaviour of 3-carbethoxy-7-hydroxy-coumarin was studied in typical hydroxylic and non-hydroxylic solvents. The colour of the fluorescence was as follows: in rectified spirit, absolute alcohol and anhydrous methyl alcohol-brilliant blue with violet tinge; in chloroform, acetone and ether—weak blue becoming deeper on the addition of a little water; in benzene—very feeble blue; in petroleum ether—almost absent.

Discussion

From the results given in Table II it is clear that the presence of a carbethoxyl, carboxyl or acetyl group in position 3 of 7-hydroxy and 7-methoxycoumarins enhances the fluorescent property of these compounds so much that they exhibit bright fluorescence even in neutral alcoholic solutions. The hydroxy compounds differ from the methoxy series in the following characteristics: (1) The former produce bright fluorescence in neutral and alkaline media and the intensity is considerably diminished in acid

TABLE I

Phenolic aldehyde	Ester condensed	Product	Gross appearance	Microscopic appearance	M.P.	Formula	Required		Found	
							% C	% H	% C	% H
Resorcylic aldehyde	Ethyl benzoyl acetate	3-benzoyl-7-hydroxy coumarin	Light pale yellow clusters	Stout needles and narrow rectangular prisms	236–37°	$C_{16}H_{10}O_4$	72·2	3·8	72·6	4·2
Orcylic aldehyde	Ethyl aceto-acetate	3-acetyl-5-methyl-7-hydroxycoumarin	Citron yellow glistening powder	Rhombic and rectangular prisms	224–25°	$C_{12}H_{10}O_4$, $\frac{1}{2}$ H_2O	63·5	4·8	63·8	5·1
,,	Ethyl benzoyl acetate	3-benzoyl-5-methyl-7-hydroxycoumarin	Pale yellow woolly clusters	Long rectangular prisms	231–32°	$C_{17}H_{12}O_4$	72·9	4·3	72·5	4·6
4-O-methyl resorcylic aldehyde	Ethyl aceto-acetate	3-acetyl-7-methoxycoumarin	Glistening lemon yellow needles	Thin rectangular plates	168–69°	$C_{12}H_{10}O_4$	66·1	4·6	65·8	4·6
,,	Ethyl benzoyl acetate	3-benzoyl-7-methoxy-coumarin	Light white clusters	Long stout fibrous needles	153°	$C_{17}H_{12}O_4$	72·9	4·3	73·2	4·2
,,	Diethyl malonate	3-carbethoxy-7-methoxy coumarin	White glistening powder	Rectangular plates	134°	$C_{13}H_{12}O_5$	62·9	4·8	62·5	4·8
		3-carboxy-7-methoxy-coumarin	White glistening flakes	Plates and prisms	195°	$C_{11}H_8O_5$	60·0	3·6	60·0	3·4

TABLE II

Colour of the Fluorescence

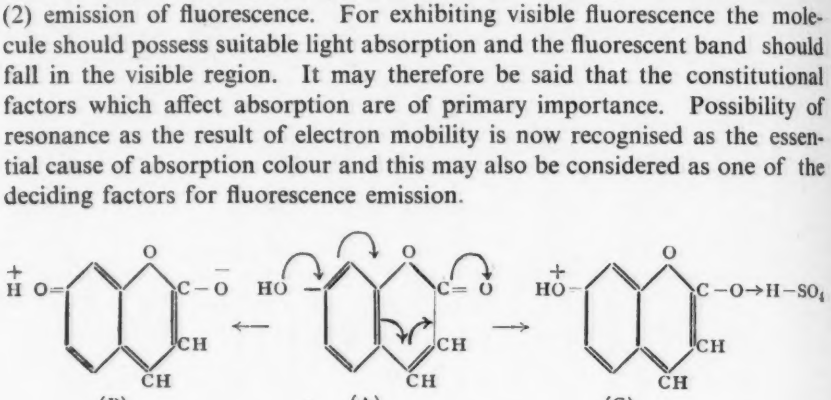
TABLE II

Colour of the Fluorescence

Compound	In concentrated sulphuric acid	In alcohol	In alcoholic solution after addition of one drop of dilute acid	In alcoholic solution after addition of one drop of dilute alkali
3-Carbethoxy-7-hydroxycoumarin[3]	Bright blue violet	Bright blue with violet tinge	Not qualitatively affected, just a bit less intense	Bright pure blue (solution is pale yellow in colour)
3-Carboxy-7-hydroxycoumarin[3] ..	,,	,,	,,	Bright pure blue (solution not coloured yellow)
3-Acetyl-7-hydroxy coumarin ..	Pale blue	Violet blue	Very pale violet	Bright pure blue (solution yellow)
3-Benzoyl-7-hydroxy-coumarin ..	Nil (solution deep yellow)	Nil (solution colour less)	Nil	Nil (even a solution in tap water has yellow colour)
3-Carbethoxy-5-methyl-7-hydroxy-coumarin[4]	Pale blue	Bright blue with violet tinge	Considerably reduced	Bright blue (solution pale yellow)
3-Carboxy-5-methyl-7-hydroxy-coumarin[4]	,,	,,	,,	,,
3-Acetyl-5-methyl-7-hydroxy-coumarin	Pale bluish green (solution pale yellow)	Blue with green tinge	Very pale violet	Bright blue with green tinge (solution yellow)
3-Benzo l-5-methyl-7-hydroxy-coumarin	Nil (solution deep yellow)	Nil (pale yellow solution)	Nil (solution colourless)	Nil (solution deep yellow ; even tap water gives pale yellow solution)
3-Carbethoxy-7-methoxycoumarin	Bright violet blue	Pale violet	Not affected	Fluorescence lost ; (solution yellow) either addition of acid or large dilution restores violet fluorescence
3-Carboxy-7-methoxycoumarin ..	,,	Violet blue	,,	Flourescence lost (solution colourless); either addition of acid or large dilution restores violet fluorescence (sodium salt sparingly soluble)
3-Acetyl-7-methoxycoumarin ..	Blue (solution pale yellow)	Very pale violet	Very pale violet	Deep yellow solution ; bright blue fluorescence on dilution with water or alcohol.
3-Benzoyl-7-methoxy-coumarin	Nil (solution deep yellow)	Nil	Nil	Nil (solution very pale yellow)

media. The reverse is the case with the latter. (2) The fluorescence of the hydroxy compounds is blue whereas that of the methoxy series is more on the violet side. The 3-benzoyl compounds differ markedly from the others. The solids as well as their solutions are markedly coloured yellow and they exhibit no visible fluorescence under any condition.

In explaining fluorescence and in looking for a correlation between it and chemical constitution it has to be borne in mind that the phenomenon has two important aspects, (1) absorption of light by the molecule and (2) emission of fluorescence. For exhibiting visible fluorescence the molecule should possess suitable light absorption and the fluorescent band should fall in the visible region. It may therefore be said that the constitutional factors which affect absorption are of primary importance. Possibility of resonance as the result of electron mobility is now recognised as the essential cause of absorption colour and this may also be considered as one of the deciding factors for fluorescence emission.



[R = H or CH_3; R′ = OH, OEt or CH_3]

Though resonance exists in umbelliferone (A) it is not sufficient to produce fluorescence. Only charged molecules present in solution in aqueous alkali or concentrated sulphuric acid exhibit this property. The structures of these molecules may be represented by (B) and (C) respectively. In 7-methoxy-coumarin, structures (A) and (C) alone are possible since dilute alkali does not react with it. The introduction of a carbonyl group in position 3 in the shape of a carbethoxyl, carboxyl or acetyl enhances resonance as shown in (D) since two carbonyl groups take part and hence these compounds fluoresce even in neutral alcoholic solution. This may be further

accentuated in the case of the 7-hydroxy compounds (R = H) by the capacity of the phenolic hydroxyl to undergo ionisation. The effect of acid in diminishing fluorescence in this case may be due to the hindrance offered by it to this ionisation. Such a possibility does not exist in regard to the 7-methoxy compounds. On the other hand the weakening of fluorescence of the methoxy compounds on adding alkali may be attributed to the influence of the negative hydroxyl ions of the alkali in preventing the polarisation of the carbonyl group and thus diminishing resonance. Further the alkaline solutions are coloured yellow and the fluorescence is not easily visible. Dilution with water not only weakens this absorption colour but it also diminishes the concentration of the hydroxyl ions and thus fluorescence is rendered again prominent.

In the case of the 3-benzoyl compounds (E) the introduction of a new benzene ring has brought about far-reaching changes. Since this ring can act as an electron sink as well as an electron source resonance is obviously increased and it is evident from the deep colour of the compounds. But the fluorescence band has either shifted to the infra-red or all emission is inhibited as the result of degradation of the absorbed light into heat.

Summary

A number of umbelliferone derivatives with acetyl, benzoyl, carbethoxyl or carboxyl groups in the 3-position have been prepared of which 6 are new. The fluorescence exhibited by these has been studied and the results are discussed.

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